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FOR THE YEAR MDCCCLIV.

VOL. 144.

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MDCCCLIV.

ADVERTISEMENT.

THE Committee appointed by the *Royal Society* to direct the publication of the *Philosophical Transactions*, take this opportunity to acquaint the Public, that it fully appears, as well from the Council-books and Journals of the Society, as from repeated declarations which have been made in several former *Transactions*, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication, than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the *Transactions* had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the Public, that their usual meetings were then continued, for the improvement of knowledge, and benefit of mankind, the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

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But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed, to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions*; which was accordingly done upon the 26th of March 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them; without pretending to answer for the certainty of the facts, or propriety of the reasonings, contained in the several papers so published, which must still rest on the credit or judgement of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body,

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upon any subject, either of Nature or Art, that comes before them. And therefore the thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society; the authors whereof, or those who exhibit them, frequently take the liberty to report and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices; which in some instances have been too lightly credited, to the dishonour of the Society.

The Meteorological Journal hitherto kept by the Assistant Secretary at the Apartments of the Royal Society, by order of the President and Council, and published in the Philosophical Transactions, has been discontinued. The Government, on the recommendation of the President and Council, has established at the Royal Observatory at Greenwich, under the superintendence of the Astronomer Royal, a Magnetical and Meteorological Observatory, where observations are made on an extended scale, which are regularly published. These, which correspond with the grand scheme of observations now carrying out in different parts of the globe, supersede the necessity of a continuance of the observations made at the Apartments of the Royal Society, which could not be rendered so perfect as was desirable, on account of the imperfections of the locality and the multiplied duties of the observer.

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Adjudication of the Medals of the Royal Society for the year 1853 by the President and Council.

The Copley Medal to Heinrich Wilhelm Dovè, for his work "On the Distribution of Heat over the Surface of the Earth."

The Royal Medal to Charles Darwin, Esq., for his works entitled "Geological Observations on Coral Reefs," "Volcanic Islands," and on "South America;" and his work, "Fossil Cirrhipeda of Great-Britain, Section Lepadidæ, Monograph of the Cirrhipeda."

(*The second* Royal Medal *was not awarded.*)

The Bakerian Lecture for 1853 was delivered by Colonel Sabine, V.P.R.S., and entitled "On the Influence of the Moon on the Magnetic Declination at Toronto, St. Helena, and Hobarton."

Adjudication of the Medals of the Royal Society for the year 1854 by the President and Council.

The Copley Medal to Professor Johannes Müller, for his important contributions to different branches of Physiology and Comparative Anatomy, and particularly for his researches on the Embryology and Structure of the Echinodermata, contained in a series of memoirs published in the Transactions of the Royal Academy of Sciences of Berlin.

A Royal Medal to Dr. Hofmann, F.R.S., for his researches in Organic Chemistry.

A Royal Medal to Dr. Hooker, F.R.S., for his researches in various branches of science, especially in Botany, as Naturalist of the Antarctic Expedition of Sir James Ross, and in an Expedition to the eastern part of the Himalaya Range, of which researches part has been published in works entitled, "The Antarctic Flora" and "The Flora of New Zealand," and in various other communications, and part is now in course of publication.

The Rumford Medal to Dr. Neil Arnott, F.R.S., author of various contributions to the elucidation of the principles and improvement of the practice of heating and ventilation, for the successful construction of a new smoke-consuming and fuel-saving fire-grate, described in the Journal of the Society of Arts of May 12, 1854.

The Bakerian Lecture for 1854 was delivered by Thomas Graham, Esq., F.R.S., and entitled, "On Osmotic Force."

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Madras.

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Senftenberg, Baron von	Prague.
Wartmann, Professor Elie	Geneva.
Younghusband, Capt., R.A.	

PHILOSOPHICAL TRANSACTIONS.

I. *On the Vibrations and Tones produced by the Contact of Bodies having different Temperatures.* By JOHN TYNDALL, *Ph.D., F.R.S., Member of the Royal Society of Haarlem, and Professor of Natural Philosophy in the Royal Institution.*

Received January 15,—Read January 26, 1854.

IN the year 1805, M. SCHWARTZ, inspector of one of the smelting-works of Saxony, having a quantity of silver in a ladle which had just solidified after melting, and wishing to hasten its cooling placed it upon a cold anvil, when to his astonishment sounds, which he compared to those of an organ, proceeded from the mass. The rumour of this discovery excited the curiosity of Professor GILBERT, the editor of GILBERT'S Annalen, and in the autumn of the same year he paid a visit to the smelting-works in question. He there learned that the piece of silver from which the sounds proceeded was cup-shaped, had a diameter of 3 or 4 inches and a depth of half an inch. GILBERT himself, under the direction of M. SCHWARTZ, repeated the experiment. He heard a distinct tone, although nothing that he could compare to the tone of an organ. He also found that the sound was accompanied by the quivering of the mass of metal, and that when the vibrations of the mass ceased, the sound ceased likewise. The Professor limited himself to the description of the phenomenon and made no attempt to explain it.

In the year 1829 Mr. ARTHUR TREVELYAN was engaged in spreading pitch with a hot plastering iron, and observing in one instance that the iron was too hot, he laid it slantingly against a block of lead which happened to be at hand. Shortly afterwards he heard a shrill note, resembling that produced on the chanter of the smaller Northumberland pipes, an instrument played by his father's gamekeeper. Not knowing the cause of the sound he thought that this person might be practising out of doors, but on going out the tone ceased to be heard, while on his return he heard it as shrill as before. His attention was at length attracted to the hot iron, which he found to be in a state of vibration, and thus discovered the origin of this strange music. In 1830 he came to Edinburgh and mentioned the fact to Dr. REID; the latter,

not knowing what SCHWARTZ and GILBERT had observed previously, regarded the phenomenon as new and recommended Mr. TREVELYAN to investigate it more fully. Mr. TREVELYAN did so; among other things he discovered the form to be given to the vibrating mass (the rocker) in order to obtain the effect with ease and certainty. The results of his numerous and well-contrived experiments were communicated to the Royal Society of Edinburgh, and were subsequently printed in the Society's Transactions.

On the 1st of April 1831 these vibrations and tones constituted the subject of a Friday evening's lecture by Professor FARADAY at the Royal Institution. The following extract from the Journal of the Institution, vol. ii. p. 120, informs us of the views of the philosopher last mentioned with respect to the cause of the tones. "As the sounds were evidently due to the rapid blows of the rocker, the only difficulty was to discover the true cause of the sustaining power by which the rocker was kept in motion, whilst any considerable difference of temperature existed between it and the block of lead underneath. This power Professor FARADAY referred to expansion and contraction, as Professor LESLIE and Mr. TREVELYAN had done generally. But he gave a minute account of the manner in which, according to his views, such expansions and contractions could produce the effect . . . . . The superiority of lead, as a cold metal, he referred to its great expansibility by heat, combined with its deficient conducting power, which is not a fifth of that of copper, silver, or gold; so that the heat accumulates much more at the point of contact in it than it could do in the latter metals, and produces an expansion proportionably greater."

Professor J. D. FORBES was present at this lecture, and by it, apparently, he was induced to undertake the further examination of the subject. On the 18th of March and on the 1st of April, 1833, the results of his inquiries were communicated to the Royal Society of Edinburgh. He dissents from the explanation supported by Professor FARADAY. The vibrations, he urges, are dependent for their existence on the difference of temperature of the two surfaces in contact; if then the heat accumulate at the surface of the cold metal, its effect will be to bring both surfaces to a common temperature and thus to stop the vibrations, instead of exalting them, as supposed by Professor FARADAY. Again, if the phenomenon be due to expansion, the greater the expansion the greater ought to be the effect; but the expansion depends upon the quantity of heat transmitted from the hot rocker to the cold block during their contact, and this again upon the conductivity of the block; so that instead of being a bad conductor, the block, to produce the greatest effect, ought to be the best conductor possible. The idea of an accumulation of heat at the surface being more favourable to the action than a rapid communication with the interior, Professor FORBES regards as an "obvious oversight*."

Having thus, to all appearance, overturned the views previously entertained, Professor FORBES proceeds to found a theory of his own. His experiments have led him

* Philosophical Magazine, Series 3, vol. iv. pages 15 and 182.

to the enunciation of certain "general laws," and these converge upon the still more general conclusion,—"that there is a repulsive action exercised in the transmission of heat from one body into another which has a less power of conducting it." This repulsion Professor FORBES considers to be "a new species of mechanical agency in heat," and he cites the remarkable experiments of FRESNEL, on the mutual repulsion of heated bodies *in vacuo*, as bearing directly upon the subject.

Such, apparently, was the unsettled state of the question when my attention was drawn towards it last summer. The possibility of the explanation offered by Professor FORBES, affording, as it seemed to do, a chance of becoming more nearly acquainted with the intimate nature of heat itself, was a strong stimulus to inquiry. I was not aware, until informed of it by my friend Professor MAGNUS, that SEEBECK had further examined the question, and substantiated the conclusions arrived at by FARADAY. On reading SEEBECK's interesting paper I found that he had already obtained many of the results which it was my intention to seek; nevertheless the portion of the subject which still remained untouched presented sufficient interest to induce me to prosecute my original idea.

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I purpose in the present memoir to examine the experimental basis of those laws which Professor FORBES regards as establishing the existence of 'a new mechanical agency in heat'; and as I am anxious to place it within the power of every experimenter to test the results to be communicated, I shall connect with each series of experiments a sufficiently exact description of the instruments made use of.

The first general law enunciated by Professor FORBES is as follows:—

"*The vibrations never take place between substances of the same nature.*"

Let us see whether this law will bear the test of experiment.

I. *Iron Rocker.*

Fig. 1, represents a sketch of the rocker; the length AC is 5·1 inches; the width AB 1·85, and the length of the stem EF is 12 inches. Fig. 2 is a transverse section

Fig. 1.

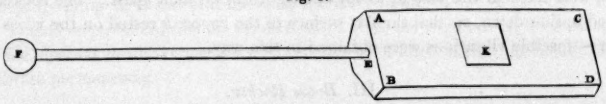

Fig. 2.

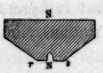

Fig. 3.

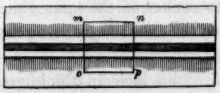

Fig. 4.

of the rocker, showing the groove underneath; the depth SN is 0·5 of an inch.

The distance *rt* is 0·35 of an inch, and it is divided into three equal spaces, the central one of which is occupied by the groove, and the other two are the surfaces which rest upon the bearer. Fig. 3 is a plan of the rocker turned upside down. The spaces *k*, fig. 1, and *mnop*, fig. 3, will, for the present, be left out of consideration.

1. The blade of a dinner knife was fixed in a vice so that the edge was horizontal. The rocker was laid upon the edge, and the stem suitably supported. On stirring the rocker a loud and musical sound commenced, and continued for a considerable time.

2. The knife was removed and a plate of sheet iron $\frac{1}{40}$th of an inch in thickness was fixed in the vice; the hot rocker was caused to rest upon the edge of the plate. On stirring the rocker, vibrations, accompanied by a musical tone, were set up as before.

3. The experiment was repeated with a second plate of iron $\frac{1}{100}$th of an inch in thickness, and a still better tone was obtained:—when the rocker rested on a *block* of iron the vibrations were not permanent.

II. *Copper Rocker.*

The pieces *k* and *mnop*, figs. 1 and 3, are plates of copper, screwed tightly on to the surface of the iron. In this way a single rocker is made to do the duty of two.

1. A plate of copper $\frac{1}{60}$th of an inch in thickness was fixed in the vice, as in the former cases; and the copper portion of the rocker was caused to rest upon it. A slight shock, imparted to the rocker, immediately excited a strong and durable tone.

2. A bit of copper foil was fixed in the vice; it was almost as flexible as stout foolscap paper, but to give it rigidity the height of it which projected above the vice was very minute. With a little care I obtained tones stronger and more musical than in the foregoing instance.

3. When the rocker was laid upon a *block* of copper no tone was obtained, and it was found that the difficulty of obtaining a tone increased as the plate made use of became thicker.

4. Instead of the plate, two wires of copper $\frac{1}{15}$th of an inch thick, and pointed with a file, were fixed in the vice at about one-eighth of an inch apart. The rocker was turned upside down, so that the flat surface of the copper *k* rested on the wires as in fig. 4:—forcible vibrations were obtained in this way.

III. *Brass Rocker.*

1. A piece of brass tube was fixed in the vice and its cylindrical surface rendered clean by a fine file. A brass rocker of the same dimensions as that represented in fig. 1, was caused to rest upon the tube; on stirring the rocker continuous vibrations succeeded.

2. A plate of brass $\frac{1}{100}$th of an inch in thickness was fixed in the vice. The rocker being laid upon the edge of the plate and stirred, stronger and more durable vibrations were obtained than in the case of the tube.

3. The experiment was repeated with a plate twice the thickness of the former; distinct vibrations were obtained. It was found in this case also that the thinner the plate, within its limits of rigidity, the more decided were the effects:—when the rocker was laid upon a *block* of brass there was no permanent vibration.

4. The rocker was turned upside down, its flat surface resting upon the points of two common brass pins; a constant rocking was the consequence.

IV. *Silver Rocker.*

This instrument was formed by attaching a piece of silver to the brass rocker used in the last experiments, exactly as the piece of copper, *mnop*, was attached to the iron rocker, fig. 1. The silver partook of the general shape of the under surface of the rocker, being bevelled off on both sides of the groove passing through its centre.

1. A strip of silver about $\frac{1}{100}$th of an inch in thickness was fixed in the vice, and the silver portion of the rocker was caused to rest upon the edge of the strip. On shaking the rocker a fine mellow musical tone was obtained.

2. A new half-crown was fixed in the vice and the rocker caused to rest upon the milled edge; no permanent vibrations were obtained. A similar difficulty was encountered with the edge of a shilling. On the edge of a sixpence, a feeble, though distinct vibration was obtained.

3. When the edges of the coins were beaten out with a hammer, and thus rendered thin, distinct vibrations were obtained with all of them. I do not assert the impossibility of obtaining vibrations on the edge of a half-crown, but merely state that with the same rocker vibrations were obtained upon a thin edge of silver, and not upon a thick one.

4. The rocker was placed against a block of silver weighing about ten ounces; no permanent vibrations were obtained.

V. *Zinc Rocker.*

The instrument is of the same size and shape as the iron rocker, fig. 1, except that the depth, SN fig. 2, is less and the mass therefore lighter*.

1. Placed upon the edge of the thinnest sheet zinc, the edge having been sharpened by a file, distinct musical tones were obtained:—on a *block* of zinc the rocker refused to vibrate permanently.

Tin Rocker.

1. A cake of tin, formed by pouring the molten metal upon a smooth flat surface, was heated and balanced upon two small protuberances of a second piece of the same metal. Continuous rockings were immediately set up. I met the mass by accident in the laboratory, and having obtained the vibrations without changing its

* Better results are obtained when the rocker is still further lightened, by scooping away part of its central mass, thus making its upper surface concave instead of flat.

shape, I did not think it necessary to strengthen the action by forming it into a regular rocker.

The number of metals capable of this action might, I doubt not, be greatly extended. Thus far we have obtained vibrations with

Iron upon iron,
Copper on copper,
Brass on brass,
Silver on silver,
Zinc on zinc,
Tin on tin,

and these, I think, are sufficient to show that *the first general law of Professor* Forbes *does not stand the test of experiment.*

Seebeck indeed had already proved the untenableness of this law. His method of experimenting has been followed in one or two of the cases above described. The placing of the heated rocker upon pointed wires is his idea. Rockings are very readily obtained in this way; but when *tones* are required, the sharp edge will, I think, in general be found preferable.

The second general law of action stated by Professor Forbes is as follows:—

"*Both substances must be metallic.*"

This is the case which first excited my attention; for even granting the final explanation given by Professor Forbes to be the true one, the necessity of the law before us does not at all follow. Previous to entering upon the present subject I had found that rock-crystal and rock-salt possessed conducting powers not much, if at all, inferior to some of the metals; and this led me to suppose that either, or both of these substances, might possibly be made to exhibit the action which the above law restricts to metals.

My first attempts failed through want of delicacy, as first attempts generally do. But a little practice suggested the means of imparting to the rocker the requisite degree of mobility. Crystals of quartz were cut in such a manner that when the rocker was laid upon them a very slight force was sufficient to cause it to oscillate. By this means I had the satisfaction of obtaining distinct vibrations from a brass rocker placed upon rock-crystal.

I refrain from entering into a more exact statement of the manner in which the crystals were cut; for subsequent experience proved that there is no difficulty in obtaining the effect, without any artificial preparation whatever.

I shall now proceed to describe the results obtained with non-metallic bodies.

1. *Rock-crystal.*—The brass rocker already described was heated and placed upon the natural edge of the prism; the stem was supported by a knife-edge, so that the rocker lay nearly horizontal: a strong tone was thus obtained.

Vibrations also followed when the rocker was laid upon the edge of the pyramid which caps the hexagonal prism.

The experiments were repeated with fumy quartz, and the same result was obtained.

2. *Fluor-spar.*—A smaller brass rocker than that last used was found to answer best with this crystal. The dimensions corresponding to AC, AB, fig. 1, were 3·8 inches and 1·25 inch respectively; while the depth was the same, or nearly so. This rocker having been placed upon the natural edge of the crystalline cube, a clear and melodious note was instantly produced. Forcible vibrations were also obtained with the larger rocker, but not so clear a tone.

The angle of the cube was cloven off so as to expose the edge of the octahedron; on this edge also vibrations were obtained.

Fortification Agate.—Distinct vibrations and tones were obtained with the large brass rocker. I found it sometimes convenient to increase the time of oscillation by laying a thin brass bar with small knobs at the ends, across the rocker—a mode of experiment due, I believe, to Mr. Trevelyan. With this precaution, in the case before us, the rocker continued swinging for nearly half an hour, and when it ceased it was under the temperature of boiling water.

Rock-salt.—The rocker used in the foregoing experiment was laid aside and a piece of rock-salt was prepared for trial. The mass was cloven so as to exhibit the surfaces of the primitive cube; and was so placed that the straight line formed by the intersection of two of the surfaces of the cube was horizontal. Previous to heating the rocker, I laid it, according to practice, upon the mass, merely to ascertain whether the arrangement was likely to answer. To my astonishment a deep musical sound commenced immediately. The temperature of the rocker was at this time far below that of boiling water, and when it had ended its song it was scarcely above a blood heat.

The heated rocker was laid upon a large boulder-shaped mass of the salt; it commenced to sing immediately. I scarcely know a substance, metallic or non-metallic, with which vibrations can be obtained with greater ease and certainty than with this mineral. To the remarkable properties which the researches of Melloni have shown to belong to rock-salt a new one may now be added.

Avanturine.—I was tempted to try this mineral from having met a piece of it possessing a clean sharp edge. The large brass rocker placed hot upon this edge gave a decided tone.

Sulphate of Potash.—Care is required with this artificial crystal, as it readily flies to pieces on the sudden communication of heat. With proper precautions, feeble, but well-established vibrations, were obtained.

Onyx.—A distinct tone.

Tourmaline.—After many trials I obtained a continuous vibration and low tone.

Fossil Wood.—Two different specimens were examined and distinct tones obtained with both of them.

Banded Agate.—Strong and continuous vibrations, when the rocker was very hot.

Chalcedony.—Loud and long-continued knockings on a knob of this mineral.

Glass.—Decided vibrations on the smooth rounded edge of the foot of a drinking-glass. Mr. TREVELYAN believed that he once obtained vibrations upon glass, but the fact is doubted by Professor FORBES. This is the only experiment on non-metallic bodies, as far as I am aware of, hitherto on record.

Earthenware.—A feeble tone, which soon ceased, was obtained on the edge of a dinner plate.

Flint.—A decided tone, though not so strong as that obtained from rock-crystal.

Lydian Stone.—Permanent vibrations.

Heliotrope.—A durable tone.

Iceland-spar.—A lighter rocker than any of those hitherto described was found necessary in experimenting with this crystal. The mass is soft, and is readily bruised by the rocker, when the latter is heavy. With a suitable instrument a continuous feeble tone was obtained.

Red Hematite.—Distinct tones were produced by several specimens of this mineral.

Arseniacal Cobalt.—A strong tone.

Meteoric Iron from Mexico.—A low musical tone.

This list might be readily extended. The substances mentioned in it were chosen on account of their accidentally presenting the conditions favourable to experiment. The principal condition is a clean even edge. Several of the minerals possessed such edges cut artificially; others possessed them naturally. In the case of chalcedony, the rocker was placed upon a rounded knob; in the case of tourmaline, one of the ridges, which usually run along the surface of the prism, served as a support; with glass and earthenware the surfaces were smooth and rounded. As a general rule however I have found an even edge best. With such an edge, and rockers similar to those described, no difficulty will be experienced in repeating and extending these experiments.

It is usual to permit the knob at the end of the handle of the rocker to rest upon a flat surface, while the instrument itself leans slantingly against the bearer. In delicate experiments I think a knife-edge is a better support for the handle, the rocker being placed horizontal, or nearly so.

Omitting the last three substances, which might, perhaps, with some justice be regarded as metallic, we find a number of exceptions to the law under consideration which far exceeds the number of bodies mentioned in the paper of Professor FORBES. *These exceptions demonstrate that the second law also is untenable.*

The third general law runs as follows:—

"*The vibrations take place with an intensity proportional (within certain limits) to the difference of the conducting powers of the metals for heat, the metal having least conducting power being necessarily the coldest.*"

The evidence adduced against the validity of the first law appears to destroy this one also; for if the vibrations are to be ascribed to a difference in the conducting powers of the rocker and bearer, then when there is no such difference there ought to be no vibrations. But we have shown, in half-a-dozen cases, that vibrations

occur when rocker and bearer are of the same metal. The same facts deprive the latter part of the third law of its significance.

I will however cite one or two experiments, in which the conditions regarded necessary by Professor Forbes were reversed, and the effect was produced notwithstanding.

1. Silver stands at the head of the conductors of heat. A copper rocker was laid upon the edge of a thin plate of this metal; strong musical notes were obtained from the arrangement.

2. Forcible vibrations were produced by placing a brass rocker upon the same silver plate.

3. A feeble, but distinct tone, was produced by the iron rocker.

4. Gold is a better conductor than brass; nevertheless strong vibrations were obtained by placing a hot brass rocker upon the edge of a half-sovereign.

These experiments are, I think, sufficient to prove the non-existence of the third law.

In the prosecution of his inquiry Professor Forbes discovered "that at least two metals were perfectly inert in either situation, namely, antimony and bismuth." Considering the explanation given, that the effects are due to the mechanical repulsion exerted by the heat in its passage from a good conductor to a bad one, the inertness of the two bodies mentioned presents a grave difficulty. Reflecting on the subject, the thought occurred to me, that if a mass of bismuth or antimony were cut so that the plane of most eminent cleavage might be vertical, the superior conductivity which the mass probably possesses in the direction of the said cleavage might aid in the production of the vibrations. I cut such a piece from a mass of antimony and fixed it in a vice, so that the horizontal edge on which the large brass rocker rested was perpendicular to the surfaces of principal cleavage. Loud and sustained vibrations were the consequence. I repeated the experiment in the case of bismuth with equal success; and after a little practice found that the precaution of cutting the substances in the manner just described was wholly unnecessary, and that tones could be obtained with facility, no matter what might be the direction in which the mass was cut.

We have thus proved antimony and bismuth to be active in one position at least; but antimony is active both as rocker and bearer. Two irregular masses, the one weighing about a pound and the other five pounds, were so filed down as to present suitable surfaces for rocking. Heated, and placed upon a flat mass of lead, both masses vibrated permanently. These experiments add their evidence to that already adduced against the third law; for antimony is a worse conductor than lead, and antimony is here the *hottest* metal.

These results appear to leave the theory of Professor Forbes without any foundation. One point only remains to be considered. Professor Faraday attributes the superiority of lead as a bearer to its great expansibility by heat, combined with its deficient conducting power. Against this view Professor Forbes argues in the ingenious manner already described. It cannot be denied that when the supporting metal is a good conductor a greater quantity of heat will pass into it during contact

than when it is a bad one. It cannot be denied that the greater the quantity of heat transmitted, the greater will be the expansion; and hence the conclusion seems unavoidable, that, if the vibration be due to expansion, both rocker and bearer, other things being equal, ought to possess the power of conduction in the highest possible degree.

Assuming then that the effects are produced by ordinary expansion, the argument of Professor Forbes stated in its severe logical form would be as follows:—

The greater the expansion the greater will be the effect; but,

The greater the conducting power the greater is the expansion: therefore,

The greater the conducting power the greater will be the effect.

This, to all appearance, is conclusive. A slight inadvertence, however, in the use of the term 'expansion' appears to deprive the argument of much of its force. In the first proposition the term means expansion *in a vertical direction*; for if this be not meant the proposition would be untrue. In the second proposition, however, it is the *total expansion* that is referred to*. Now supposing the conductivity of the bearer to be infinite; that is to say, that the quantity of heat which it receives from the rocker during contact is instantaneously distributed equally throughout its entire mass, then, although the total expansion might be very great, there would be no *local* expansion at all, and therefore none of the effects in question. The expansion we require is a sudden elevation of the point where the rocker comes into contact with the bearer, and it is manifest that "a rapid communication with the interior" may, by suddenly withdrawing the heat from the point where it is communicated, almost extinguish the requisite elevation, and thus prevent the vibrations. This appears to be the precise reason why Professor Forbes has failed to obtain the numerous results described in the foregoing pages. His bearers were of such a form that the mass of matter immediately surrounding the point of contact quickly abstracted the heat communicated to that point, and thus destroyed the condition upon which the vibrations depend. The success of the experiments described in this memoir depends on the precaution, that the abstraction of heat was prevented, to some extent, by reducing the bearers to laminæ and mere spikes; and the fact that a thin edge gave a better tone than a thick one thus receives a full explanation. These considerations, I think, render it clear that the cause of the superiority of lead assigned by Professor Faraday is by no means an "oversight." On the other hand it would not be safe to affirm generally, nor has it been affirmed by the philosopher last mentioned, that the less the conducting power the greater will be the effect. In the case of glass and earthenware the vibrations soon come to an end, for the requisite difference of temperature between rocker and bearer, as anticipated by Professor Forbes, soon ceases. Perfect non-conductibility would be just as inefficacious as perfect conductibility, and the region of practical results lies between these two extremes.

* Seebeck makes use of the same argument.—J. T.

Royal Institution, January, 1854.

II. *Theory of the Reciprocal Action between the Solar Rays and the different Media by which they are reflected, refracted, or absorbed; in the course of which various optical laws and phenomena are elucidated and explained.* By JOSEPH POWER, *M.A., Fellow of Clare Hall, and Librarian of the University of Cambridge: Member of the Cambridge Philosophical and Antiquarian Societies, and Foundation Fellow of the Society of Northern Antiquarians at Copenhagen. Communicated by the Rev.* J. CAPE, *F.R.S.*

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1. FOR the train of thought which suggested the following considerations, I am more particularly indebted to the researches of Professor DRAPER of New York, contained in his remarkable work, "On the Organisation of Plants, the Chemical Effects of the Solar Rays, &c.," 2nd edit., New York, 1845. His experiments tend to show that the law of action and reaction, which prevails so generally in other departments of nature, is no less true in all the varied phenomena of the sunbeam, so that the latter cannot be reflected, refracted, much less absorbed, without producing some change upon the recipient medium.

2. Whilst however I acknowledge my obligations to the author for the information I have derived from his excellent work, I wish carefully to guard against the inference that I agree with him as to the necessity of admitting the existence of more than one imponderable, being strongly of opinion that all the effects of the solar rays may be attributed to some or other of the infinite variety of undulations of which the universal ether is capable, and which in the case of the sunbeam are impressed upon it by vibrations at the surface of the sun.

3. The *vis viva*, which has its origin in these vibrations, is transmitted through the ether with the velocity of light in extremely minute undulations of different lengths and periods.

If then a sunbeam, fraught with a vast variety of such undulations, be incident upon a medium so constituted that its particles are capable of vibrating in unison, or even in harmonic consonance less perfect than unison, with some or other of the ethereal vibrations of the incident beam, it must necessarily happen that one system of vibrations will be called into existence by the other according to the laws of *resonance*.

There may be a difficulty in explaining, but there can be no doubt of the fact, that the *vis viva* due to such induced vibrations, like that which is due to the vibra-

tions of heat, may become more or less persistent in the medium; producing at one time the phenomenon of fixed chemical action, at another time that of permanently latent heat, at another time that less permanently latent or retarded heat, at another time that of coloration and absorption, at another time that of phosphogenic action. The remarkable phenomena lately discovered by Professor STOKES seem closely allied to the latter, differing however in the circumstance that they cease to exist the moment the exciting rays are withdrawn. Guided by analogy, I am inclined to think that these phenomena will be found hereafter to possess some slight though insensible duration, while I regard all action which is really momentary as expending itself upon the passing rays as they emerge in the form of reflected or refracted rays.

But all these effects, of whatever kind, I regard as due to one and the same cause, which can, I conceive, be no other than the expenditure or distribution of the *vis viva* originally derived from the sun, and conveyed by the ether unchanged in amount.

4. By the term *vis viva* is here meant, the sum of the vibrating molecules each multiplied by the square of its velocity, a quantity which, by the usual dynamical theories, is constant, when we neglect the distant attractions (whose effects must be insensible on the all-but-imponderable ether), and take into account only the mutual actions of the molecules upon each other, in all cases, most certainly, when the molecules after being put in motion return to the same places which they occupied before their motion commenced, and there resume their former state of rest. It is extremely probable that this is the case in the propagation of a solar ray through the ethereal spaces, as we know that it is the case when a small vibratory pulse is in the course of propagation along a stretched wire, as also in every case of propagated undulations in which we can examine a the circumstances. We may further argue that, if the particles of an ethereal space, originally at rest, after transmitting a state of motion from a preceding to a succeeding space, were not again reduced to rest, the space first mentioned will continue to originate fresh motions, which would be propagated in one or more directions, *after the former wave has passed*; the ethereal space, therefore, after transmitting a luminous wave, would either continue for a while to be self-luminous, which is contrary to all we know of light, or else to be the source of vibrations of a different nature to those which set it in motion; a supposition, which is so great a departure from simplicity, as to be extremely improbable; it is further, as before stated, opposed to all the analogies presented by cases of propagated undulations in which the circumstances are known. There is therefore scarcely room for a doubt that the *vis viva* of the luminous waves is transmitted through the ethereal spaces unchanged in quantity.

There is yet another way of establishing this principle, which may be more satisfactory to some minds.

Let p, p' denote the *vires vivas* due to a luminous wave as it spreads out spherically with the velocity (a), and crosses successively over the spherical surfaces $4\pi r^2$, $4\pi r'^2$ in equal times $\left(\frac{\lambda}{a}\right)$, r, r' being any two distances from the origin of the light regarded

as a point, and λ the length of the undulation. Then, if ϖ be the area of the pupil, properly directed towards the luminous point at the successive distances r and r', $\frac{\varpi p}{4\pi r^2}$ and $\frac{\varpi p'}{4\pi r'^2}$ will be the quantities of *vis viva* which pass through the pupil in equal times, and being condensed on the retina produce the sensation of light with brightnesses proportional to their magnitudes. This accords with the views of all writers on the subject of physical optics. On the other hand, we know by experience, that these brightnesses are as $\frac{1}{r^2}$ and $\frac{1}{r'^2}$, consequently $p=p'$; the ether intermediate to the two spheres in transmitting the luminous wave has therefore delivered over the *vis viva* unchanged in quantity.

5. Let us now consider what will become of the *vis viva* when the luminous wave is incident upon the plane surface of a refracting medium. I shall confine my attention in the present communication to a singly refracting isotropical medium, amongst the comparatively grosser particles of which the incomparably more subtle and more numerous particles of the ether are supposed to be diffused in a different state of density to that which prevails in the surrounding spaces, such altered density being due to the attractions or repulsions which the particles of the medium exercise on those of the ether.

This being premised, we may regard the expenditure of the *vis viva* as of two kinds, according as it is distributed to the particles of the ether, giving rise to the reflected and refracted rays, or to the particles of the refracting medium. If it be expended solely on the ether, the sum of the *vires vivæ* of the reflected and refracted waves ought to be exactly equal to the *vis viva* of the incident wave; but if a portion of the *vis viva* be communicated to the particles of the medium, the *vis viva* of the incident wave ought to surpass the sum of the *vires vivæ* of the reflected and refracted waves by a certain excess.

6. The object with which the present inquiry commenced was to take into account the effect of such supposed excess, in the hope of arriving at some explanation of the Stokesian phenomena. The remarkable result I have obtained, that *every loss of* vis viva *will be accompanied by a diminution of the refractive index*, is quite in the direction of the author's own idea of "a change of refrangibility;" but I confess it throws no light on the change of *period*, which it is also necessary to account for. The latter, I am inclined to think, is due to an action of the nature of *harmonic resonance*, and from some calculations which I have made, I think it probable that the light produced in the Stokesian experiments may be due to resonant vibrations excited in the medium, which are about a major or minor third lower in pitch than those of the invisible rays producing them, the medium afterwards communicating those vibrations to the ether as a new source of light.

7. Some apology may be required for borrowing from the language of music, terms explanatory of phenomena which cannot be heard, and in some cases neither heard nor seen; but critical taste must be prepared to yield a general licence to physical inquirers to indulge in such catachreses of language, whenever they are called for by

the generalisation of ideas, for the expression of which, without such an alternative, a new language must necessarily be invented.

8. The mode of procedure which seemed most likely to lead to a successful result, was to assume in the first instance the hypothesis that the *vis viva* is expended solely on the reflected and refracted rays, and afterwards to modify, if possible, the steps of the process so as to adapt them to the hypothesis that a portion of it is expended on the medium, regarded as distinct from the ether by which it is permeated.

9. In adopting the more simple hypothesis I was really startled by the formula at which I arrived in the course of the investigation, for not only did the general or Cartesian law of refraction spring out most unexpectedly, as if by magic, but those very same expressions for the intensity of the reflected rays, which were first discovered by Fresnel, and subsequently verified by the experiments of Brewster and Arago, were an immediate consequence of the formulæ.

But while my results are in perfect harmony with experience so far as the latter has proceeded, at the same time they differ from those of Fresnel in some particulars. In the first place the index of refraction is not the simple quotient of the velocities of undulation, but of those velocities each multiplied by the density of the ether in the corresponding medium. In the second place, the vibrations of the ethereal particles are performed *in* the plane of polarization (and not perpendicular to that plane, as Fresnel supposed), agreeing therein, amongst others, with Maccullagh, Naumann, and the earlier researches of Cauchy, but opposed to the more recent investigations of the latter and to the experimental determination of Professor Stokes*. Further, the expressions for the intensities of the *refracted* rays differ slightly in other respects from those of Fresnel, as given in Airy's Tracts; I am not aware that these intensities have been tested by experiment, nor are the refracted rays so readily accessible to the experimenter as the reflected rays. I may be permitted however to claim, in favour of my own results, that in no one instance do I have recourse to forced analogies or gratuitous hypotheses, the process I have pursued standing in need of no such help. I adopt indeed universally the fundamental hypothesis that the vibrations on which light depends, and consequently those of the reflected and refracted as well as of the incident rays, are strictly transverse to the directions of the rays. I admit that this hypothesis, considered *à priori*, must be regarded as perfectly arbitrary; but it gains evidence, almost amounting to certainty, *à posteriori*, when we take into account the immense variety of phenomena connected with the polarization and depolarization of light, of which it affords a simple and satisfactory explanation. I am aware of the difficulties which have caused other theorists to modify this hypothesis in case of the reflected and refracted rays; but I do not think that those difficulties should be objected to me, who approach the problem in an entirely different way, and who take into account circumstances which have been neglected by them, namely, the vibrations communicated to the medium itself. It is not surprising that such difficulties should occur in a dynamical theory which takes no account of such

* Cambridge Transactions, vol. ix. part 1.

communication of vibrations; indeed the *statical* condition of two contiguous ethereal media of different densities is impossible, unless we take into account the mutual statical actions between the particles of the ether and those of the crystal which it is supposed to permeate; much more are the *dynamical* conditions likely to be fraught with inconsistency, unless we take into account the mutual dynamical actions of those particles. I think it is considerably in favour of the present mode of viewing the problem, that no difficulties of the kind under consideration are found to present themselves.

10. I confine my attention, as I have before stated, to an isotropical singly refracting medium, like glass or water, though I think, if I had more time at my disposal, I could extend the theory to doubly refracting crystals. A very simple integration gives me a general expression for the *vis viva* of an elementary cycloidal wave, in terms of the amplitude and the constants of the periodical function. By help of this I obtain two equations of *vis viva*, one for a wave whose vibrations are in the plane of incidence, and the other for a wave whose vibrations are perpendicular to that plane, both vibrations being transverse to the axis of the ray. By the principle of superposition, these two equations will hold true simultaneouely when the above waves are regarded as the components of one and the same wave. I obtain three other equations between the amplitudes, from the simple consideration that a particle situated in the common surface of the two media cannot vibrate in more than one way at once. Of these three equations two involve the amplitudes of the first component wave, and the third those of the second.

The five equations serve to determine, in terms of the angle of incidence and the component amplitudes of the incident wave, the five following quantities, namely, the angle of refraction, the two component amplitudes of the reflected wave, and those of the refracted wave.

11. By the help of FOURIER's theorem we may decompose any form of undulation, extending between given limits, into a series of elementary cycloidal undulations, varying in wave-length, amplitude and orientation; and, again, a wave whose orientation deviates from the plane of incidence, or a plane perpendicular to this passing through the axis of the ray, may be resolved into two, one in each of the above planes, which I shall term respectively the primary and secondary planes.

Let θ be the angle of incidence of a cylindrical beam or incident ray; and let

$$y = h \sin \frac{2\pi}{\lambda} (at + x)$$

$$z = k \sin \frac{2\pi}{\lambda} (at + x + c)$$

represent the displacements due to any one of its cycloidal elementary waves, resolved parallel to the primary and secondary plane, x being the distance from the point of incidence measured along the axis of the ray, (a) the velocity of undulation, and t the time measured from some epoch anterior to incidence.

From these two equations we may readily derive the following,

$$\frac{y^2}{h^2}-2\cos\left(\frac{2\pi c}{\lambda}\right).\frac{yz}{hk}+\frac{z^2}{k^2}=\sin^2.\left(\frac{2\pi c}{\lambda}\right),$$

giving for the motion of an ethereal particle, in general, an ellipse having its centre in the axis of the ray and its plane perpendicular to that axis.

The constant c determines the difference of phase of the two component waves; if the phases be coincident, we have $c=0$, in which case the above equation becomes

$$z=\frac{k}{h}y.$$

The particle, therefore, performs its vibration in a straight line inclined to the axis of y, that is, *to the plane of incidence* at an angle whose tangent is $\frac{k}{h}$. I shall call this the angle of orientation: denoting it by γ, we get

$$\tan\gamma=\frac{k}{h}$$

$$\tan 2\gamma=\frac{2\frac{k}{h}}{1-\frac{k^2}{h^2}}=\frac{2hk}{h^2-k^2}.$$

In general it is not difficult to show, by the usual method of transformation of coordinates, that the major axis of the elliptic orbit, whose equation has been exhibited above, makes with the plane of incidence an angle of orientation (γ) determined by the equation

$$\tan 2\gamma=\frac{2hk}{h^2-k^2}\cos\left(\frac{2\pi c}{\lambda}\right).$$

If $h=k$, $\gamma=\frac{\pi}{4}$ in both cases; the linear radius of vibration and the axis major of the elliptical vibration are therefore inclined to the plane of incidence at an angle of 45°.

In the particular case of $h=k$, and $c=\frac{\lambda}{4}$,

$$\tan 2\gamma=\frac{0}{0};$$

and is therefore indeterminate, but in that case the equation becomes

$$y^2+z^2=h^2.$$

each particle therefore describes a circle about a point in the axis of the ray, and all traces of orientation disappear.

It is needless to state that the three cases, which have here been briefly discussed, are those usually distinguished as belonging to plane polarized, elliptically polarized, and circularly polarized light.

12. By the theory of superposition of small motions we are at liberty to consider

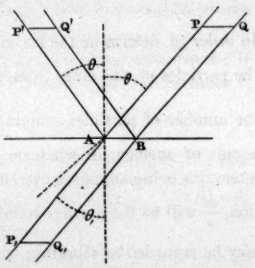
each component wave separately. Let us first take the primary component whose displacement is in the plane of incidence and determined by the equation

$$y=h\sin\frac{2\pi}{\lambda}.(at+x).$$

In order to determine the *vis viva* due to one undulation, let α be the distance of the particles of the ether from each other; the medium being isotropical, $\frac{1}{\alpha}$ will be the number of particles contained in a unit of line, and $\frac{1}{\alpha^2}$ the number contained in a unit of surface, in whatever direction the line or surface may be turned: the interval α being supposed extremely small compared with λ the length of an undulation, $\frac{dx}{\alpha}$ will be the average number of particles contained in a portion dx of λ, which may be regarded as vibrating with the common velocity $\frac{2\pi h a}{\lambda}\cos\frac{2\pi}{\lambda}(at-x)$ found by differentiating the expression for y with respect to t. The *vis viva* of a single line of vibrating particles at the given instant (t), therefore $=\frac{4\pi^2h^2a^2}{\alpha\lambda^2}\int\cos^2.\frac{2\pi}{\lambda}(at+x)dx$ from $x=x$ to $x=x+\lambda$. This is easily found to be $\frac{2\pi^2h^2a^2}{\lambda\alpha}$; and it is worthy of remark, though this is no more than we ought naturally to expect, that the result is independent of the phase at the beginning and end of the integral. The same will be true of every length λ of particles which constitute the incident cylindrical beam, whatever may be the nature of the phase at the two extremities. Let ω be the oblique section of this beam made by the common surface of the two media; then $\omega\cos\theta$ is the transverse section of the incident beam made by a plane perpendicular to its axis, and $\frac{\omega\cos\theta}{\alpha^2}$ is the number of ethereal particles in this section. Hence to obtain the *vis viva* of one undulation of the incident beam we have only to multiply the *vis viva* of each line of particles $\frac{2\pi^2h^2a^2}{\lambda\alpha}$ by $\frac{\omega\cos\theta}{\alpha^2}$, and the result is $\frac{2\pi^2h^2a^2\omega\cos\theta}{\lambda\alpha^3}$, which holds true whether the particles be in the same phase for the whole extent of each transverse section, as, I think, is commonly supposed, or whether the phase be supposed to vary from particle to particle in such transverse section, according to some continuous law depending on the original vibrations at the surface of the sun or other origin of the beam; it being understood of course that at a given instant the same *type* or system of phases will recur for sections separated from each other by the interval λ. There will be the same recurrence of type for sections made by planes inclined to the beam at any given angle θ, and separated from each other by the perpendicular interval $\lambda\cos\theta$; and, further, the *vis viva* contained between two such planes will be the same as before, since every line of particles will have as much *vis viva* added at one extremity as is cut off at the other, when the cutting planes are turned from the transverse position through the angle θ. If θ be the angle of inci-

dence, the cutting planes become parallel to the surface of separation of the two media.

Hence if we take AP=λ=BQ, and take a section PQ of the incident beam parallel to AB (ω) the surface of separation, the *vis viva* of PABQ will have for its expression $\frac{2\pi^2h^2a^2\omega\cos\theta}{\lambda\alpha^3}$.



If instead of λ we wish to introduce the period of undulation (τ), or the number of undulations in a unit of time (ν), since $\frac{\lambda}{a}=\tau=\frac{1}{\nu}$, the expression becomes $\frac{2\pi^2h^2}{\alpha^3\tau}.a\omega\cos\theta$, or $\frac{2\pi^2h^2}{\alpha^3}.a\nu\omega\cos\theta$.

13. In the same way*, if h' and $h_{,}$ be the amplitudes of the reflected and refracted rays, $\theta_{,}$ the angle of refraction, $\alpha_{,}$ the distance of the ethereal particles from each other in the second medium, and $a_{,}$ the velocity of undulation in that medium, the *vires vivæ* of the same wave after the reflexion and refraction has been completed will be severally represented by $\frac{2\pi^2h'^2}{\alpha^3}a\nu\omega\cos\theta$ and $\frac{2\pi^2h_{,}^2}{\alpha_{,}^3}a_{,}\nu\omega\cos\theta_{,}$, ν being taken the same as before, inasmuch as phases of any given kind, the nodal points for instance, will be transmitted across the surface of separation just as rapidly as they arrive, so far as regards the number transmitted in a given time, but with different velocities of undulation a and $a_{,}$ in the two media. Hence, on the supposition that no *vis viva* is lost by the rays, we shall have, omitting common factors,

$$\frac{h^2a\cos\theta}{\alpha^3}=\frac{h'^2a\cos\theta}{\alpha^3}+\frac{h_{,}^2a_{,}\cos\theta_{,}}{\alpha_{,}^3}.$$

14. Any particle in the surface of separation will be at one and the same moment performing its phase to the incident ray with the transverse velocity $\frac{2\pi ha}{\lambda}\cos\frac{2\pi at}{\lambda}$, or $2\pi h\nu\cos(2\pi\nu t)$, and to the reflected and refracted rays with the transverse velocities $2\pi h'\nu\cos(2\pi\nu t)$, $2\pi h_{,}\cos(2\pi\nu t)$; and since this particle cannot move in more than one way at once, it is clear that the two latter must be equivalent to the former, according to the laws of composition of velocities, which is the same as that of forces.

Hence, omitting the common factors, the amplitudes $h'h_{,}$ of the reflected and refracted rays will be statically equivalent to h, the amplitude of the incident ray, regard being had to their several directions. If, therefore, we resolve $h'h_{,}$ in the direction of h and perpendicular to that direction, the sum of the two former components will equal h, and the two latter components will destroy each other.

There is no difficulty in pursuing this process, but I prefer the following which

* It is scarcely necessary to remark, that, for the reflected and refracted waves, $at-x$ should be written in the place of $at+x$ in the expressions for the displacement, but the sign of x has no influence on the result of the integration.

leads to the same results, and gives a geometrical meaning to the language employed. By a well-known theorem in statics, if one force be equivalent to two others, and lines be drawn *making any given angle* with the directions of the three forces, the sides of the triangle intercepted by these lines will respectively represent the forces in magnitude and sign.

Let us agree to regard as positive those motions which tend to the right hand of a person supposed to be swimming on the plane of incidence in the direction in which any one of the three rays proceeds. Now the directions of the three rays themselves being those of the three excursions $hh'h_1$, *each turned from right to left through a right angle*, it follows from the theorem just enunciated, that the sides of a triangle which are respectively parallel to the three rays, will properly represent the transverse velocities in magnitude and sign.

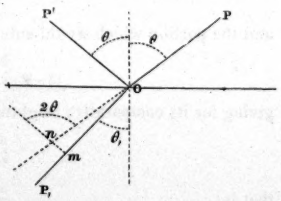
Let PO, OP' and OP$_1$ be the directions of the incident reflected and refracted rays; take m any point in the latter, and draw mn parallel to OP', meeting PO produced in n.

By the rules of composition, On is equivalent to Om and mn, and since all three are measured in the direction in which the rays proceed, their signs must all be regarded as positive. Consequently h, h' and h_1 have the same sign and are severally proportional to On, Om, mn, and therefore to sin Omn, sin Onm, sin nOm; that is, to sin $(\theta+\theta_1)$, sin 2θ, and sin $(\theta-\theta_1)$.

We have, therefore,

$$\frac{h'}{h}=\frac{\sin(\theta-\theta_1)}{\sin(\theta+\theta_1)}$$

$$\frac{h_1}{h}=\frac{\sin 2\theta}{\sin(\theta+\theta_1)}.$$



15. These equations, combined with the former, serve to determine h' h_1 θ_1.

Substituting the above values in the equation of No. (13), put under the form

$$\frac{a\cos\theta}{\alpha^3}\left\{1-\frac{h'^2}{h^2}\right\}=\frac{a_1\cos\theta_1}{a_1^3}\frac{h_1^2}{h^2}$$

we get

$$\frac{a\cos\theta}{\alpha^3}\{\sin^2(\theta+\theta_1)-\sin^2(\theta-\theta_1)\}=\frac{a_1\cos\theta_1}{a_1^3}4\sin^2\theta\cos^2\theta.$$

Now

$$\begin{aligned}&\sin^2(\theta+\theta_1)-\sin^2(\theta-\theta_1)\\&=\{\sin(\theta+\theta_1)+\sin(\theta-\theta_1)\}\{\sin(\theta+\theta_1)-\sin(\theta-\theta_1)\}\\&=2\sin\theta.\cos\theta_1.2\cos\theta.\sin\theta_1.\end{aligned}$$

Therefore, substituting and dividing by the common factors, we get

$$\frac{a\sin\theta_1}{\alpha^3}=\frac{a_1\sin\theta}{\alpha_1^3},$$

or

$$\sin\theta_1=\frac{\alpha^3}{\alpha_1^3}.\frac{a_1}{a}\sin\theta.$$

This equation, combined with

$$h'=h\frac{\sin(\theta-\theta_1)}{\sin(\theta+\theta_1)}$$

$$h_1=h\frac{\sin 2\theta}{\sin(\theta+\theta_1)},$$

completely determines the reflected and refracted rays. The *vis viva* of the reflected ray will thus have for its expression

$$\frac{2\pi^2 h^2}{\alpha^3} a\nu\omega \cos\theta . \frac{\sin^2(\theta-\theta_1)}{\sin^2(\theta+\theta_1)}.$$

If ϖ be the area of the pupil, we must alter the above in the ratio $\varpi : \omega\cos\theta$, the section of the reflected beam, which gives

$$\frac{2\pi^2 h^2}{\alpha^3} a\nu\varpi \frac{\sin^2(\theta-\theta_1)}{\sin^2(\theta+\theta_1)}$$

for the quantity of *vis viva* which enters the eye and is afterwards condensed on the retina; the corresponding expression for the incident ray is

$$\frac{2\pi^2 h^2}{\alpha^3} a\nu\varpi.$$

If then we denote the brightness of the incident ray by 1, that of the reflected ray will be represented by

$$\frac{\sin^2(\theta-\theta_1)}{\sin^2(\theta+\theta_1)}.$$

In like manner the *vis viva* of the refracted ray is

$$\frac{2\pi^2 h^2}{\alpha_1^3} a_1\nu\omega \cos\theta_1 \frac{\sin^2(2\theta)}{\sin^2(\theta+\theta_1)};$$

and the portion which would enter the eye, could it be placed so as to receive it, is

$$\frac{2\pi^2 h^2}{\alpha_1^3} a_1\nu\varpi . \frac{\sin^2(2\theta)}{\sin^2(\theta+\theta_1)},$$

giving for its comparative brightness the expression

$$\frac{\alpha^3}{\alpha_1^3}\frac{a_1}{a}\frac{\sin^2(2\theta)}{\sin^2(\theta+\theta_1)},$$

that is,

$$\frac{\sin\theta_1}{\sin\theta} . \frac{4\sin^2\theta.\cos^2\theta}{\sin^2(\theta+\theta_1)},$$

or

$$\frac{4\cos^2\theta.\sin\theta\sin\theta_1}{\sin^2(\theta+\theta_1)}.$$

16. Let us now take the component wave whose vibrations are performed in the secondary plane. Any displacement being represented by the equation

$$z = k\sin\frac{2\pi}{\lambda}(at+x+c),$$

proceeding exactly as before, we shall have, on the supposition that no *vis viva* is lost,

$$\frac{k^2 a\cos\theta}{\alpha^3} = \frac{k'^2 a\cos\theta}{\alpha^3} + \frac{k_1^2 a_1\cos\theta_1}{\alpha_1^3}.$$

The motion of a particle in the surface of separation regarded as performing its phase to the incident ray is $2\pi k\nu\cos(2\pi\nu t)$, which, as before, must be statically equivalent to $2\pi k'\nu\cos(2\pi\nu t)$ and $2\pi k_1\nu\cos(2\pi\nu t)$; but the directions of these three motions

being perpendicular to the plane of incidence and therefore parallel to each other, we have not two equations, as in the last case, but only one, namely,

$$k=k'+k_1;$$

but θ_1 being already determined, we have sufficient data for determining k' and k_1.

Putting the equation of *vis viva* under the form

$$\frac{a\cos\theta}{\alpha^3}.\{k^2-k'^2\}=\frac{a_1\cos\theta_1}{\alpha_1^3}\{k-k'\}^2,$$

we see that it is satisfied by making either $k-k'=0$,

or
$$\frac{a\cos\theta}{\alpha^3}(k+k')=\frac{a_1\cos\theta_1}{\alpha_1^3}(k-k').$$

The first solution gives $k'=k$ and $k_1=0$, so that the ray is totally reflected; the *vis viva* of the reflected ray being equal to that of the incident ray.

The second solution gives in conjunction with

$$\frac{a}{\alpha^3}\sin\theta_1=\frac{a_1}{\alpha_1^3}\sin\theta,$$

$$\sin\theta\cos\theta.(k+k')=\sin\theta_1\cos\theta_1(k-k'),$$

or
$$(\sin 2\theta+\sin 2\theta_1)k'=(\sin 2\theta_1-\sin 2\theta)k,$$

whence we obtain
$$k'=-k.\frac{\sin(2\theta)-\sin(2\theta_1)}{\sin(2\theta)+\sin(2\theta_1)}$$

$$=-k.\frac{\tan(\theta-\theta_1)}{\tan(\theta+\theta_1)}$$

$$k_1=k-k'=k.\frac{\tan(\theta+\theta_1)+\tan(\theta-\theta_1)}{\tan(\theta+\theta_1)},$$

or
$$k_1=k.\frac{2\sin 2\theta}{\sin 2\theta+\sin 2\theta_1}.$$

The *vis viva* of the reflected ray is therefore

$$\frac{2\pi^2k^2}{\alpha^3}a\nu\omega\cos\theta.\frac{\tan^2(\theta-\theta_1)}{\tan^2(\theta+\theta_1)},$$

and its relative brightness, compared with that of the incident wave, namely,

$$\frac{2\pi^2k^2}{\alpha^3}a\nu\omega\cos\theta, \quad \text{is} \quad \frac{\tan^2(\theta-\theta_1)}{\tan^2(\theta+\theta_1)}.$$

The *vis viva* of the refracted wave is

$$\frac{2\pi^2k^2}{\alpha_1^3}a_1\rho\omega\cos\theta_1\frac{4\sin^2 2\theta}{(\sin 2\theta+\sin^2\theta_1)^2};$$

and its relative brightness is obtained by first multiplying it by $\frac{\varpi}{\omega\cos\theta_1}$ and then dividing it by

$$\frac{2\pi^2k^2}{\alpha^3}.a\nu\omega\cos\theta.\frac{\varpi}{\omega\cos\theta}\text{ (as in No. 15)},$$

giving for result $$\frac{\alpha^3}{\alpha_1^3}\frac{a_1}{a}\cdot\frac{4\sin^2 2\theta}{(\sin 2\theta+\sin 2\theta_1)^2},$$

that is, $$\frac{4\sin^2(2\theta)\sin\theta_1}{\sin\theta(\sin 2\theta+\sin 2\theta_1)^2},$$

or $$\frac{16\cos^2\theta\cdot\sin\theta\sin\theta_1}{(\sin 2\theta+\sin 2\theta)^2}.$$

The rule to be followed in selecting the proper solution out of two possible ones, is to take that which causes the ray to deviate as little as possible from its original direction; this is at least the most natural course, and accords with experience in accounting for the phenomenon of polarization, as we shall immediately see; the contrary choice would leave that phenomenon unexplained; we have therefore no alternative but to adopt the second solution.

17. It may be observed, by the way, that the expressions of the intensities

$$\frac{\sin^2(\theta-\theta_1)}{\sin^2(\theta+\theta_1)},\quad\frac{\tan^2(\theta-\theta_1)}{\tan^2(\theta+\theta_1)},$$

which I have found for the reflected rays whose vibrations occur respectively in the primary and secondary planes, exactly coincide with those which Fresnel has found for the reflected rays whose vibrations are respectively performed in the secondary and primary planes; while the expressions for the intensities of the refracted rays, with the same interchange of planes, only approximately coincide with those deduced by Fresnel.

18. If $\theta+\theta_1=\frac{\pi}{2}$ the expression for the secondary reflected ray vanishes; hence it follows that the incident beam, resulting from the superposition of the two components, after reflexion at the particular angle which satisfies the condition $\theta+\theta_1=\frac{\pi}{2}$, will produce a reflected ray of the primary class, that is to say, a ray whose vibrations are performed entirely *in* the plane of incidence.

If μ be the index of refraction, we have

$$\mu=\frac{\sin\theta}{\sin\theta_1}=\frac{a_1^3 a}{\alpha^3 a_1}=\frac{\varrho a}{\varrho_1 a_1},$$

ϱ, ϱ_1 denoting the densities of the ether as it exists in the two media, for which the rates of undulation are respectively a, a_1.

When $\theta_1=\frac{\pi}{2}-\theta$, we have $\sin\theta_1=\cos\theta$, and therefore $\tan\theta=\mu$, the law (first discovered by Brewster) which determines what is called the polarising angle, agreeably to experience.

But after incidence at this angle, the beam resulting from the superposition of the two component rays, will, after reflexion, consist entirely of vibrations performed in the plane of incidence, and not, as Fresnel supposed, in a plane at right angles to this.

19. Let $\gamma, \gamma', \gamma_1$ denote generally the orientations of the major axes of the molecular orbits of the incident, reflected and refracted rays, which, in the case of plane polarized rays, are the same as the angles which the planes of vibration make with the plane of incidence (see No. 11). First, for a plane polarized incident ray, in which case $c=0$, we have

$$\tan\gamma=\frac{k}{h},\quad \tan\gamma'=\frac{k'}{h'},\quad \tan\gamma_1=\frac{k_1}{h_1}.$$

Substituting for $h'\,k'\,h_1\,k_1$ their values, we find

$$\tan\gamma'=-\frac{k}{h}\frac{\cos(\theta+\theta_1)}{\cos(\theta-\theta_1)}=-\tan\gamma.\frac{\cos(\theta+\theta_1)}{\cos(\theta-\theta_1)}$$

$$\tan\gamma_1=\frac{k}{h}.\frac{2\sin(\theta+\theta_1)}{\sin 2\theta+\sin 2\theta_1}=2\tan\gamma.\frac{\sin(\theta+\theta_1)}{\sin 2\theta+\sin 2\theta_1}.$$

These formulæ show the shiftings of the plane in which the vibrations are performed, and consequently of the plane perpendicular to this, which is usually called the plane of polarization. The first agrees with the formula, p. 361 of AIRY's Tracts, γ, γ' being of course the complements of the angles there denoted by α, β, which formula is there stated to have been verified by numerous observations of BREWSTER and ARAGO. If the incident ray be elliptically polarized, the expressions for $\tan\gamma$, $\tan\gamma'$, $\tan\gamma_1$ are of course more complicated.

I have stated in No. 11, though for brevity the proof has been omitted, that in the general case,

$$\tan 2\gamma=\frac{2hk}{h^2-k^2}\cos\left(\frac{2\pi c}{\lambda}\right).$$

If we put

$$\frac{hk}{h^2-k^2}\cos\left(\frac{2\pi c}{\lambda}\right)=\beta,$$

we shall have

$$\frac{2\tan\gamma}{1-\tan^2\gamma}=2\beta,$$

whence

$$\tan^2\gamma+\frac{1}{\beta}\tan\gamma-1=0,$$

and

$$\tan\gamma=-\frac{1}{2\beta}\pm\sqrt{\left(1+\frac{1}{4\beta^2}\right)}.$$

To determine which sign ought to be used, we may observe that the expression ought to reduce itself to $\frac{k}{h}$ when $c=0$, as in the former case. But making $c=0$, we have

$$\beta=\frac{hk}{h^2-k^2},$$

and the root becomes

$$-\frac{h^2-k^2}{2hk}\pm\sqrt{\left(1+\frac{(h^2-k^2)^2}{4h^2k^2}\right)},$$

which reduces itself to $\frac{k}{h}$ or $-\frac{h}{k}$, according as we take the upper or lower sign. The

upper sign must therefore be taken, and we shall have generally without ambiguity,

$$\tan\gamma=-\frac{h^2-k^2}{2hk}\sec\frac{2\pi c}{\lambda}+\sqrt{\left(1+\frac{(h^2-k^2)}{4h^2k^2}\sec^2\frac{2\pi c}{\lambda}\right)}.$$

The other value expresses the orientation of the *axis minor*, since the product of the two values is -1.

20. It may be worth observing, that if one of these values had been mistaken for the other, it would have made a difference of 90° in the direction of vibration in the case of a plane polarized ray, for which $c=0$, and we should thus be brought back to the hypothesis of Fresnel. I mention this merely to show how easily error may be introduced in proceeding from one formula to another, and I would suggest the possibility that the discrepancies of different theorists on this particular point may in some instances be removed by a closer attention to the meaning of ambiguous signs.

21. From the last expression for $\tan\gamma$ we may derive those for $\tan\gamma'$ and $\tan\gamma_1$; for this purpose we have merely to write $h'k'$, or h_1k_1 in the place of hk, and afterwards to substitute for $h'k'h_1k_1$ their values in terms of hk and θ. The results would probably admit of simplification in some degree, but I shall content myself with having pointed out the mode of obtaining them.

22. I now proceed to the case in which a portion of the *vis viva* of the incident ray is supposed to be communicated to the refracting medium during the same shock which splits up the incident beam into the reflected and refracted rays.

Denoting by p the *vis viva* of the primary component of the incident ray, and by $p'p_1p_{11}$ the expenditure of the same upon the reflected ray, the refracted ray and the medium respectively, and denoting the angles of incidence and refraction and the different amplitudes as before, we shall have

$$p=p'+p_1+p_{11},$$

or putting

$$\frac{p_{11}}{p_1}=s,$$

$$p=p'+(1+s)p_1.$$

But we have already found by integration,

$$p=\frac{2\pi^2h^2}{\alpha^3}a\nu\omega\cos\theta$$

$$p'=\frac{2\pi^2h'^2}{\alpha^3}a\nu\omega\cos\theta$$

$$p_1=\frac{2\pi^2h_1^2}{\alpha_1^3}a_1\nu\omega\cos\theta_1.$$

Consequently

$$\frac{h^2a\cos\theta}{\alpha^3}=\frac{h'^2a\cos\theta}{\alpha^3}+\frac{(1+s)h'^2}{\alpha_1^3}a_1\cos\theta_1.$$

We shall further have, as before,

$$\frac{h'}{h}=\frac{\sin(\theta-\theta_1)}{\sin(\theta+\theta_1)}$$

$$\frac{h_1}{h}=\frac{\sin(2\theta)}{\sin(\theta+\theta_1)}.$$

We have therefore exactly the same equations to combine as before, with the sole exception that $\frac{a_i}{\sqrt[3]{1+s}}$ occupies the place of a_i; we have therefore only to make this simple change in the value of $\sin\theta_i$, and we obtain

$$\sin\theta_i=(1+s).\frac{\alpha^3}{\alpha_i^3}\frac{a_i}{a}\sin\theta$$

$$p=\frac{2\pi^2h^2}{\alpha^3}a\nu\omega\cos\theta$$

$$p'=\frac{2\pi^2h^2}{\alpha^3}a\nu\omega\cos\theta.\frac{\sin^2(\theta-\theta_i)}{\sin^2(\theta+\theta_i)}$$

$$p_i=\frac{2\pi^2h^2}{\alpha_i^3}a_i\nu\omega\cos\theta_i.\frac{\sin^2(2\theta)}{\sin^2(\theta+\theta_i)},$$

with the same expressions for the comparative brightness as before. See No. 16.

23. The first of the above equations, compared with the Cartesian law of refraction, regarded as an experimental truth, shows that s is independent of θ; in fact

$$s=\frac{a_i^3a}{\alpha^3a_i}.\frac{\sin\theta_i}{\sin\theta}-1,$$

and since by the Cartesian law $\frac{\sin\theta_i}{\sin\theta}$ is independent of θ, it follows that s is also independent of θ. This quantity must therefore be regarded as a certain coefficient of absorption, depending mainly on the constitution of the crystal and the period of the incident ray, possibly also in some degree on the orientation of the ray, or the position of the plane in which its vibrations are performed, with regard to certain fixed planes in the crystal, or refracting medium, whether solid or fluid. The theoretical determination of this coefficient can only result from a more perfect theory of resonance than has hitherto been given, and it is hoped that some of the great modern analysts will turn their attention in this direction.

If we denote the former refractive index $\frac{\alpha_i^3}{\alpha^3}\frac{a}{a_i}$, or $\frac{\varrho a}{\varrho_i a_i}$, by μ, as before, and the altered refracted index $\frac{\alpha^3}{(1+s)\alpha_i^3}.\frac{a}{a_i}$, or $\frac{1}{1+s}\frac{\varrho a}{\varrho_i a_i}$, by μ_i, we shall have

$$\mu_i=\frac{\mu}{1+s}.$$

This very simple formula, now given for the first time, demonstrates the rule I have before enunciated, namely,

The solar rays can exercise no action upon any medium through which they are transmitted without an accompanying diminution of the refractive index.

24. To estimate the effect of this diminution upon the intensities (i', i_i) of the reflected and refracted rays, unity as before representing the intensity of the incident primary ray, we have

$$i'=\frac{p'}{p}=\frac{\sin^2(\theta-\theta_i)}{\sin^2(\theta+\theta_i)}$$

$$i_i = p_{i\frac{\varpi}{\omega\cos\theta_i}} \div p_{\frac{\varpi}{\omega\cos\theta}}$$

$$= \frac{\cos\theta}{\cos\theta_i}.\frac{p_i}{p}$$

$$= \frac{\sin^2(2\theta)}{\sin^2(\theta+\theta_i)}.\frac{\alpha^3 a_i}{\alpha_i^3 a}$$

$$= \frac{\sin^2(2\theta)}{\sin^2(\theta+\theta_i)}.\frac{1}{1+s}.\frac{\sin\theta_i}{\sin\theta},$$

that is,

$$i_i = \frac{4}{1+s}.\frac{\cos^2\theta.\sin\theta.\sin\theta_i}{\sin^2(\theta+\theta_i)}.$$

Let us now proceed to the case of the secondary component wave.

Denoting by $q\,q'\,q_i$ the *vires vivæ* of the incident, reflected and refracted rays, and by q_{ii} the *vis viva* communicated to the medium, we have

$$q = q' + q_i + q_{ii};$$

and denoting $\frac{q_{ii}}{q_i}$ by s',

we have $$q = q' + (1+s').q_i.$$

We have, further,

$$q = \frac{2\pi^2 k^2}{\alpha^3} a v\omega\cos\theta$$

$$q' = \frac{2\pi^2 k^2}{\alpha^3} a v\omega\cos\theta$$

$$q_i = \frac{2\pi^2 k_i^2}{\alpha_i^3} a_i v\omega\cos\theta_i.$$

Consequently $$\frac{k^2 a\cos\theta}{\alpha^3} = \frac{k'^2 a\cos\theta}{\alpha^3} + \frac{k_i^2 a_i\cos\theta_i(1+s')}{\alpha_i^3},$$

with which must be combined, as before, the equation

$$k = k' + k_i.$$

These equations lead to the same results as before, except that $\frac{\alpha_i}{\sqrt[3]{1+s'}}$ occupies the place of α_i, giving, besides the case of total reflexion, the equation

$$\frac{a\cos\theta}{\alpha^3}(k+k') = \frac{a_i\cos\theta_i(1+s')}{\alpha_i^3}(k-k').$$

Combining with this the equation

$$\sin\theta_i = (1+s).\frac{\alpha^3 a_i}{\alpha_i^3 a}\sin\theta,$$

we get $$(1+s)\sin\theta\cos\theta(k+k') = (1+s').\sin\theta_i\cos\theta_i.(k-k'),$$

whence $$k'\{(1+s)\sin 2\theta + (1+s')\sin 2\theta_i\} = k.\{(1+s')\sin 2\theta_i - (1+s).\sin 2\theta\},$$

or

$$k' = -k.\frac{(1+s)\sin 2\theta - (1+s')\sin 2\theta_i}{(1+s)\sin 2\theta + (1+s')\sin 2\theta_i},$$

whence $$k_i=\frac{2k.(1+s)\sin 2\theta}{(1+s)\sin 2\theta+(1+s')\sin 2\theta_i}.$$

Consequently $$q=\frac{2\pi^2k^2}{\alpha^3}\,av\omega\cos\theta$$

$$q'=\frac{2\pi^2k^2}{\alpha^3}\,av\omega\cos\theta\left\{\frac{(1+s)\sin 2\theta-(1+s').\sin 2\theta_i}{(1+s)\sin 2\theta+(1+s')\sin 2\theta_i}\right\}^2$$

$$q_i=\frac{2\pi^2k^2}{\alpha_i^3}\,a_iv\omega\cos\theta_i\left\{\frac{2(1+s).\sin 2\theta}{(1+s)\sin 2\theta+(1+s')\sin 2\theta_i}\right\}^2.$$

25. If j' j_i denote the comparative brightness of the reflected and refracted rays, that of the incident secondary ray being represented by unity, we shall have

$$j'=\frac{q'}{q}=\left\{\frac{(1+s)\sin 2\theta-(1+s').\sin 2\theta_i}{(1+s)\sin 2\theta+(1+s')\sin 2\theta_i}\right\}^2$$

$$j_i=q_i.\frac{\varpi}{\omega\cos\theta_i}\div q\frac{\varpi}{\omega\cos\theta}=\frac{\cos\theta}{\cos\theta_i}.\frac{q_i}{q}$$

$$=\frac{\alpha^3}{\alpha_i^3}.\frac{a_i}{a}.\frac{k_i^2}{k^2}=\frac{1}{1+s}.\frac{\sin\theta_i}{\sin\theta}.\frac{k_i^2}{k^2},$$

or $$j_i=\frac{4}{1+s}.\frac{\sin\theta_i}{\sin\theta}.\left\{\frac{(1+s)\sin 2\theta}{(1+s)\sin 2\theta+(1+s')\sin 2\theta_i}\right\}^2.$$

If then j' be $=\frac{\tan^2(\theta-\theta_i)}{\tan^2(\theta+\theta_i)}$, as the experiments of BREWSTER and ARAGO would lead us to infer, in all such cases at least we must have $s'=s$. In fact, $\frac{\tan(\theta-\theta_i)}{\tan(\theta+\theta_i)}$ being equivalent to $\frac{\sin 2\theta-\sin 2\theta_i}{\sin 2\theta+\sin 2\theta_i}$, we could not have exact agreement between theory and experiment unless

$$\frac{(1+s)\sin 2\theta-(1+s')\sin 2\theta_i}{(1+s)\sin 2\theta+(1+s')\sin 2\theta_i}=\frac{\sin 2\theta-\sin 2\theta_i}{\sin 2\theta+\sin 2\theta_i},$$

that is, unless $$(1+s)\sin 2\theta.\sin 2\theta_i-(1+s')\sin 2\theta.\sin 2\theta_i$$

$$=-(1+s)\sin 2\theta\sin 2\theta_i+(1+s')\sin 2\theta\sin 2\theta_i,$$

that is, unless $$2(1+s)=2(1+s'),\text{ or }s=s'.$$

Neither without this condition would j' vanish when $\theta+\theta_i=\frac{\pi}{2}$, or $2\theta_i=\pi-2\theta$, for in that case the expression for j' becomes $\left\{\frac{s-s'}{2+s+s'}\right\}^2$.

26. It is extremely natural to suppose that the effect upon the medium is mainly, if not entirely, operated by the refracted ray in its passage into the medium, *after* its separation from the reflected ray; and as s and s' denote the ratios $\frac{p_{ii}}{p_i}$, $\frac{q_{ii}}{q_i}$, that is to say, the ratio, for each case, in which the *vis viva* entering the medium distributes itself between the particles of the medium and the particles of the ether interfused amongst them, we ought to expect that in an isotropical medium, like that under

consideration, this ratio of distribution should be independent of orientation, and consequently the same for both the primary and secondary refracted waves.

27. I am not disposed however to leap too suddenly to the conclusion that the reflected ray in the action of turning through the angle $\pi-2\theta$ has no influence in imparting *vis viva* to the medium*; though it must be conceded that in all cases where the brightness of the reflected rays accurately follows the laws of FRESNEL as tested by BREWSTER and ARAGO, the reflected ray has no sensible influence on the medium; for were it otherwise, we ought in an accurate theory of resonance to find a difference in the values of s and s', as we do in the intensities of the primary and secondary waves, both reflected and refracted, and we have already seen that such difference of values will vitiate the law for the secondary reflected ray. It makes all the difference in the world, whether the *vis viva* be supposed to be communicated to the medium at the very instant of the shock, or immediately afterwards; in the first case it will be due partly to the reflected and partly to the refracted rays, in the latter case it will be due almost entirely to the refracted rays. In all cases, however, it is natural to suppose that the refracted rays are chiefly instrumental, and this is indicated by the equality of s and s' in isotropical media, without which equality the laws of FRESNEL, BREWSTER and ARAGO, could not, according to the present theory, be *accurately*, though they might very well be *approximately* true, as in fact they would be if s s', though different from each other, were very small compared with unity. In clear transparent media, where there is little absorption, s and s' are probably very small, and such being the case, the above law of brightness ought to hold, independent of the equality $s=s'$.

28. I return now to the expressions for the refractive index

$$\mu=\frac{\varrho a}{\varrho_1 a_1}$$

$$\mu_1=\frac{1}{1+s}\cdot\frac{\varrho a}{\varrho_1 a_1}=\frac{\mu}{1+s}.$$

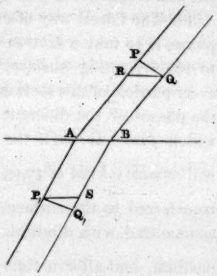
In the first place, it will be remarked that these differ from the value which is usually adopted, namely, $\frac{a}{a_1}$.

I confess I always considered that the usual mode of deducing this value from the *spread of the wave*, which in fact does not spread, was more elegant than conclusive. It is connected, if I mistake not, with the idea that the transverse front of a wave of light, as of a wave of sound, consists of particles all of which are in the same phase;

* Nevertheless it is worth observing, that at the critical angle (compare No. 39), in the case of $s=s'$, it results from the formulæ that the absorbing power of the medium has no effect in diminishing the *vis viva* when the ray is turned through an angle $\pi-2\theta$ in the operation of reflexion, and this is true both for the primary and secondary rays. I am therefore inclined to think, and other considerations confirm me in that opinion, that the absorbing medium acts something like a *file* in thinning off the absorbed portions of the ray, and requires that the ray should penetrate into its substance before it can exercise any absorbing action upon it.

the equation $\frac{\sin\theta}{\sin\theta_1}=\frac{a}{a_1}$ may, in fact, be derived from that hypothesis, without any consideration of the spread of the wave.

To make this appear, suppose PQ, a transverse section of the incident beam, to be all in the same phase of vibration, and after a certain time to have undulated into the position P_1Q_1, having been previously refracted by the surface AB. The time from P through A to P_1 will be



$$\frac{PA}{a}+\frac{AP_1}{a_1},$$

that from Q through B to Q_1 will be

$$\frac{BQ}{a}+\frac{BQ_1}{a_1}.$$

Equating these and transposing, we get

$$\frac{PA-BQ}{a}=\frac{BQ_1-AP_1}{a_1},$$

that is, drawing QR and P_1S parallel to AB,

$$\frac{PR}{a}=\frac{Q_1S}{a_1};$$

and since $RQ=AB=P_1S$,

$$\therefore\quad \frac{PR}{RQ}=\frac{a}{a_1}\cdot\frac{Q_1S}{P_1S}.$$

But $$\frac{PR}{RQ}=\cos PRQ=\sin\theta,$$

and $$\frac{Q_1S}{P_1S}=\frac{\sin SP_1Q}{\sin P_1Q_1S}=\sin\theta_1 \text{ if } P_1Q_1S=90°,$$

and only on that supposition.

Hence the equation $$\sin\theta=\frac{a}{a_1}\sin\theta_1$$

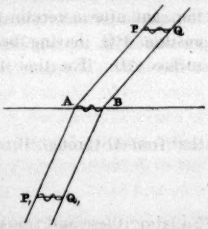
expresses the condition that P_1Q_1S is a right angle, in other words, that the direction BQ_1 of the refracted wave is perpendicular to the section of similar phase to PQ.

Now though this may be true with regard to sound, we have no reason, beyond a precarious analogy, to assume that it is true with regard to light. Indeed I think the hypothesis of a similarity of phase extending over the whole of a transverse section of the ray, whether it be the incident or refracted ray, is quite untenable; for let us consider how light is generated.

29. Light appears to be generated by the action upon the ether of the superficial particles of a vibrating body, whether those vibrations have their origin in the process of combustion, as in the flame of a candle, or in some other way, as in the case of phosphorus, the electric light, &c. The vibrations of these superficial particles must be performed *in* that superficies, otherwise they could not impart transverse vibrations to the ether in contact with them: and such being the case, it is highly

improbable, indeed next to impossible, that one uniform phase should extend over more than a very minute portion of superficies at a given instant, consistently with the conditions of continuity.

30. The fairest way of considering the subject without assuming the uniformity of phase, is to take a section of the incident ray PQ parallel to the refracting surface, and therefore $=\omega$, and upon every particle of this section to erect ordinates representing the phases of the different particles: the rippled surface which passes through the extremities of these ordinates will possess a kind of type, which after the time $\frac{PA}{a}$ will be transferred to the surface AB, through which it will be transmitted, with diminished intensity, into the refracting medium, and after a time $\frac{AP_i}{a_i}$ will be brought into the position P_iQ_i parallel to AB and PQ.



Presented under this point of view, the question affords no hold whatever for the determination of θ_i, and I think I am entitled to conclude that the formula

$$\sin\theta_i=\frac{a_i}{a}\sin\theta,$$

or

$$\mu=\frac{a}{a_i},$$

rests on no other foundation than an uncertain analogy drawn from the theory of sound, whereas the demonstrations I have given of the formulæ

$$\mu=\frac{\varrho a}{\varrho_i a_i}=\frac{\sin\theta}{\sin\theta_i},$$

$$\mu_i=\frac{1}{1+s}\frac{\varrho a}{\varrho_i a_i}=\frac{\sin\theta}{\sin\theta_i}$$

are quite independent of such analogy, and are true whatever may be the type of the rippled surface at the front of the waves.

I may mention, by the way, that I think it arises from the existence of such a rippled front of wave, that the fringes of interference, which border the margin of a small aperture, upon which a conical pencil of light is incident, are found to vanish when the aperture exceeds a very small limit; in fact, when the aperture is enlarged so as to admit a comparatively large chequered surface of the wave's front, the several portions destroy each other's effect by interference; but when the aperture is so small as only to admit a portion which presents a uniformity of phase, then the fringes present themselves and admit of the usual explanation. The hypothesis of a rippled front is therefore not only the most probable when we consider the origin of the beam, but it accounts simultaneously for the non-spread of the wave and the disappearance of the fringes when the aperture is large.

It may perhaps be urged in favour of the hypothesis of uniformity of phase in the

front of the wave, that it is necessary, in order to account for a succession of pulses on the retina, giving for different values of λ the impression of different colours analogous to different musical notes in the phenomenon of sound.

To this I reply, that the *phases of maxima vis viva* will succeed with equal rapidity in both cases, which is a complete answer to the objection.

In fact, if we adopt the hypothesis of a rippled front, the *vis viva* due to any transverse section as it enters the pupil, will have for its expression an integral of the form

$$B_1 \cos^2 \frac{2\pi}{\lambda}(at+c_1)+B_2 \cos^2 \frac{2\pi}{\lambda}(at+c_2)+B_3 \cos^2 \frac{2\pi}{\lambda}(at+c_3)+\&c.,$$

which, writing $\frac{1+\cos 2u}{2}$ in the place of $\cos^2 u$, and expanding each term, will give an expression of the form

$$A+B\cos\left(\frac{4\pi at}{\lambda_1}\right)+C\sin\left(\frac{4\pi at}{\lambda}\right),$$

that is, of the form $$A+A_1\cos\left(\frac{4\pi}{\lambda}A_2\right)\cos\frac{4\pi at}{\lambda}+A_1\sin\frac{4\pi}{\lambda}A_2\sin\frac{4\pi at}{\lambda},$$

or $$A+A_1\cos\frac{4\pi}{\lambda}(at+A_2),$$

or $$A-A_1+2A_1\sin^2\frac{2\pi}{\lambda}(at+A_2),$$

whose maximum value, $(A+A_1)$ (as also its minimum value $(A-A_1)$), recurs after intervals $\frac{\lambda}{a}, \frac{2\lambda}{a}$, &c., as is easily seen; these intervals, in fact, hold for phases of any given denomination, just as in the case of any single elementary portion of the front of the wave.

31. Let us now consider the effect of the divisor $1+s$ in the formula

$$\mu_1=\frac{1}{1+s}\cdot\mu=\frac{1}{1+s}\cdot\frac{\varrho a}{\varrho_1 a_1},$$

since $$s=\frac{p_{II}}{p_I}=\frac{\textit{vis viva}\text{ communicated to the medium}}{\textit{vis viva}\text{ of the refracted ray}}.$$

We see, that, according as the absorption is greater or less, the values of s may range between infinity and zero; corresponding to which μ_1 will range between zero and μ, the refractive index when there is no absorption.

But the equation $$\sin\theta_1=\frac{1}{\mu_1}\sin\theta=\frac{1+s}{\mu}\sin\theta,$$

shows that θ_1 will $=\frac{\pi}{2}$ as soon as

$$\frac{1+s}{\mu}\sin\theta=1,$$

or $$\sin\theta=\frac{\mu}{1+s}.$$

Hence if s be considerable, θ must be small in order that there may be a refracted

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ray, and if $\sin\theta$ exceed the critical value $\frac{\mu}{1+s}$, there will be no refracted ray, but the incident light will be totally reflected without any diminution of intensity, but with a change of phase (compare No. 39, and the Note to No. 42 at the end of this paper). Hence we see the possibility of particular rays, on which the medium exerts a powerful absorbing action at small angles of incidence, being totally reflected at larger incidences, whilst the remainder of the incident beam is partly refracted, the refracted and reflected light thus being of completely different colours. Specimens of coloured glass partaking of this property are not uncommon, and I have recently been shown a glass which is deep blue seen by reflected light, and reddish brown by refracted light, an effect which Professor STOKES, who showed me the specimen, assures me is not of the nature of *fluorescence*, the name he has finally chosen for the phenomena discovered by himself.

At the other limit, for which $s=0$, $\sin\theta_i$ attains its minimum value $\frac{1}{\mu}\sin\theta$; the rays, of which no portion has been absorbed, therefore emerge on the most refracted side of the spectrum; the same thing appears from the expression $\mu_i=\frac{\mu}{1+s}$, which shows that the refractive index is then a maximum.

32. Although it is possible in this manner to account for a considerable range of spectrum extending, with rapidly decreasing intensity, from the most refracted end, where the rays have suffered least absorption and where the intensity is the greatest, towards the least refracted end, where the intensity decreases without limit, nevertheless there is nothing in this theory which necessarily connects the degree of refraction with the colour, or more generally speaking, the period of the ray.

Experience shows that the most refracted rays have the smallest period; if then we would account for the chromatic dispersion in this way, we must admit that media are more acted upon by the rays of longer period, than by rays of shorter period, by the red than by the violet; but this is contrary to experience. The effect of absorption upon the index of refraction must therefore be regarded as antagonistic to the chromatic dispersion.

33. M. CAUCHY has, I consider, given a satisfactory theory of chromatic dispersion, which is perfectly consistent with every thing which has been advanced in the present theory. But I claim for the latter that it gives a satisfactory account of the phenomena of absorption and the spectral spaces discovered by FRAUNHOFER, and commonly known by the name of FRAUNHOFER's lines, especially when taken in connexion with the consideration of *luminous resonance*, to which subject, I think, the attention of scientific men is here directed for the first time.

In fact, according to the laws of resonance, those rays will act most forcibly on the medium, which find amongst the particles of the latter some capable of vibrating in unison, or in harmonic consonance less perfect than unison, with themselves, the unison of course giving rise to by far the most energetic action, but the other consonances producing effects more decided as the coincidences of phase are more frequent;

we see therefore in general why particular rays should be selected for absorption, without any insensible gradation, and why some lines of absorption, those corresponding to unison for example, should be more strongly marked than others; and these preliminaries being conceived, then comes the equation

$$\sin\theta_l=(1+s)\frac{\varrho_l}{\varrho^a}\sin\theta,$$

which explains how those rays which undergo absorption are turned out of their places and deflected towards the less refracted end of the spectrum, and in some cases, though with intensities so diminished as to be imperceptible, far beyond the limits of the visible spectrum. In fact as s increases, the above equation shows that θ_l increases. The refracted ray is therefore turned more from the normal, or deviates less from its original course than it would do if there were no absorption, in which case $s=0$. The intensities of the reflected and refracted rays, both in the primary and secondary planes, will of course be diminished by the loss of *vis viva*, as is further apparent from the expressions which have been obtained for i', i_l, j' and j_l in Nos. 24 and 25, namely,

$$i'=\frac{\sin^2(\theta-\theta_l)}{\sin^2(\theta+\theta_l)},\quad i_l=\frac{4}{1+s}\,\frac{\cos^2\theta\sin\theta\sin\theta_l}{\sin^2(\theta+\theta_l)},$$

$$j'=\left\{\frac{(1+s)\sin 2\theta-(1+s')\sin 2\theta_l}{(1+s)\sin 2\theta+(1+s')\sin 2\theta_l}\right\}^2$$

$$j_l=\frac{4}{1+s}\cdot\frac{\sin\theta_l}{\sin\theta}\cdot\left\{\frac{(1+s)\sin 2\theta}{(1+s)\sin 2\theta+(1+s')\sin 2\theta_l}\right\}^2,$$

where it may be observed that i_l and j_l diminish rapidly as s increases. Without the turning action above mentioned, the lines of absorption might exist indeed in a less marked manner, but the turning action fairly dismisses the weakened rays out of their places, and these places, if occupied at all, will be occupied by stray rays of a different colour from their immediate neighbours, presenting a faint tinge of the colour which has been turned from a remote space on the more refracted end of the spectrum. And this, I consider, is the true explanation of the phenomenon discovered by Brewster, and cited by Draper, p. 85; that *red light exists in the violet spaces of the solar spectrum and blue light in the red*: provided the red light in the violet spaces be regarded as the extreme violet, deflected towards the purple part of the spectrum; for the extreme violet rays, to my own eyes at least, scarcely differ in colour from the extreme red.

In the celebrated Mémoire of M. Cauchy's (1836, cited by Beer, Einleitung in die höhere Optik, p. 209, and reproduced in the Exercices d'Analyse Mém. tom. i. p. 288), the velocity of undulation is given by a rapidly converging series of the form

$$a^2=A_0+A_2\cdot\frac{\alpha^2}{\lambda^2}+A_4\,\frac{\alpha^4}{\lambda^4}+\&c.,$$

in which I have thought it right not to include α^3, α^4, &c. under the unknown constants A_3, A_4, so as to exhibit to the eye the rapidity of convergence. As a first approximation, we have

$$a=\sqrt{A_0},$$

and in order that a may be greater for the smaller wave lengths, as experience shows it is, A_2 must be positive.

If we wish to introduce in the place of λ the *note-number* ν, or the number of vibrations performed in a unit of time, since $\nu=\frac{a}{\lambda}$, we have

$$a^2=A_0+\frac{A_2}{a^2}\cdot\alpha^2\nu^2+\frac{A_4}{a^4}\cdot\alpha^4\nu^4+\&c.;$$

and since a^2, a^4 occur in the denominators, it will be sufficient to write for them the first approximate values A_0, A_0^2, &c., thus we get

$$a^2=A_0+\frac{A_2}{A_0}\alpha^2\nu^2+\frac{A_4}{A_0^2}\alpha^4\nu^4+\&c.$$

Cauchy found by comparing theory with experiment that the two foremost terms of his series were sufficient to account for the chromatic dispersion. We shall have, therefore, a sufficiently accurate value of a by extracting the square root of this series to the exclusion of terms involving ν^4, ν^6, &c. This value is

$$a=\sqrt{A_0}+\frac{1}{2}\frac{A_2\alpha^2\nu^2}{A_0\sqrt{A_0}},$$

for which we may write $a=f+g\nu^2$.

We shall have a similar expression for the second medium,

$$a_1=f_1+g_1\nu^2.$$

Consequently $$\mu=\frac{\varrho a}{\varrho_1 a_1}=\frac{\varrho(f+g\nu^2)}{\varrho_1(f_1+g_1\nu^2)},$$

which again may be represented approximately under the form $B+C\nu^2$, B and C being two constants which can only be known by experiment; but I shall adhere to the other more significant form.

Hence we obtain for the refractive index of rays, which have undergone partial absorption,

$$\frac{\sin\theta}{\sin\theta_1}=\mu_1=\frac{\mu}{1+s}=\frac{1}{1+s}\cdot\frac{\varrho(f+g\nu^2)}{\varrho_1(f_1+g_1\nu^2)},$$

whence $$\sin\theta_1=\frac{1}{\mu_1}\sin\theta=(1+s)\cdot\frac{\varrho_1(f_1+g_1\nu^2)}{\varrho(f+g\nu^2)}\sin\theta.$$

34. Though the expressions for $p'p_1q'q_1$ (see No. 22 and 24) remain unchanged in *form*, their values will of course be affected by the change of θ_1, which they involve. It would be needless to write their expressions over again, but it may be convenient for the sake of photometrical comparison to exhibit the ratios of *vires vivæ*

$$\frac{p'}{p}\,\frac{p_1}{p}\,\frac{q'}{q}\,\frac{q_1}{q},$$

which are immediately derivable from them. They are as follows:—

$$\frac{p'}{p}=\frac{\sin^2(\theta-\theta_1)}{\sin^2(\theta+\theta_1)}$$

$$\frac{p_1}{p}=\frac{1}{1+s}\cdot\frac{\sin 2\theta\cdot\sin 2\theta_1}{\sin^2(\theta+\theta_1)}$$

$$\frac{q'}{q}=\left\{\frac{(1+s)\sin 2\vartheta-(1+s')\sin 2\vartheta_l}{(1+s)\sin 2\vartheta+(1+s')\sin 2\vartheta_l}\right\}^2$$

$$\frac{q_l}{q}=\frac{4.(1+s).\sin 2\vartheta.\sin 2\vartheta_l}{\{(1+s)\sin 2\vartheta+(1+s')\sin 2\vartheta_l\}^2}.$$

If for isotropical media we suppose $s'=s$, the two last formulæ become

$$\frac{q'}{q}=\frac{\tan^2.(\vartheta-\vartheta_l)}{\tan^2(\vartheta+\vartheta_l)}$$

$$\frac{q_l}{q}=\frac{4}{1+s}.\frac{\sin 2\vartheta.\sin 2\vartheta_l}{\{\sin 2\vartheta+\sin 2\vartheta_l\}^2}.$$

35. Lastly, if γ, γ', γ_l denote, as before, the orientations of the compound rays, regarded as plane polarized, that is according to the present theory, as performing their vibrations *in* a plane making the angles γ, γ', γ_l with the plane of incidence, we shall have

$$\tan\gamma=\frac{k}{h}$$

$$\tan\gamma'=\frac{k'}{h'}=\frac{k'}{k}.\frac{h}{h'}\tan\gamma=$$

$$=-\tan\gamma.\frac{(1+s)\sin 2\vartheta-(1+s')\sin 2\vartheta_l}{(1+s).\sin 2\vartheta+(1+s')\sin 2\vartheta_l}.\frac{\sin(\vartheta+\vartheta_l)}{\sin(\vartheta-\vartheta_l)}$$

$$\tan\gamma_l=\frac{k_l}{h_l}=\frac{k_l}{k}.\frac{h}{h_l}\tan\gamma$$

$$=\frac{2.(1+s)\sin 2\vartheta}{(1+s)\sin 2\vartheta+(1+s')\sin 2\vartheta_l}.\frac{\sin(\vartheta+\vartheta_l)}{\sin 2\vartheta}\tan\gamma$$

or
$$\tan\gamma_l=\frac{2(1+s)\sin(\vartheta+\vartheta_l)}{(1+s)\sin 2\vartheta+(1+s')\sin 2\vartheta_l}.\tan\gamma.$$

If $s'=s$, we get
$$\tan\gamma'=-\frac{\tan.(\vartheta-\vartheta_l)}{\tan(\vartheta+\vartheta_l)}.\frac{\sin(\vartheta+\vartheta_l)}{\sin(\vartheta-\vartheta_l)}=-\frac{\cos(\vartheta+\vartheta_l)}{\cos(\vartheta-\vartheta_l)}\tan\gamma$$

$$\tan\gamma_l=\frac{2\sin(\vartheta+\vartheta_l)}{\sin 2\vartheta+\sin 2\vartheta_l}.\tan\gamma,$$

the same expressions which we obtained on the supposition that there was no absorption, and which have been tested by Brewster and Arago.

36. A most interesting application of this theory is the explanation it affords of the rotatory phenomena of polarization exhibited by certain liquids, as also by certain solids, some specimens of quartz, for instance, which are distinguished from each other by the known appellations of right-handed and left-handed quartz.

Let us suppose that the liquid (a solution of sugar or of honey, for instance, both of which are found to possess this property) is divided by horizontal sections at a small vertical distance $\partial\xi$ from each other, ξ being the depth below the surface of the fluid. Though there is no refraction or deviation as the rays pass from one stratum to another, nothing prevents us from making $\vartheta_l=\vartheta$ in the formulæ just found, which gives

$$p'=0, \qquad p_l=\frac{p}{1+s},$$

$$q'=\left\{\frac{s-s'}{2+s+s'}\right\}^2 q, \qquad q_1=\frac{4(1+s)}{(2+s+s')^2}q,$$

$\tan\gamma'=-\infty$, except when $s'=s$, in which case $\tan\gamma'=\frac{0}{0}$.

Further, $$\tan\gamma_1=\frac{2(1+s)}{2+s+s'}\cdot\tan\gamma.$$

We see therefore that there is no reflected ray of the first class, nor any of the second class if $s'=s$; in that case $\tan\gamma_1=\tan\gamma$, and $q_1=q$. The *vis viva* communicated to the fluid arises therefore entirely from the primary component wave, which imparts to it the *vis viva* $\frac{s}{1+s}\cdot p$; the orientation remains in this case unchanged; but if s' differs from s the case is different; in that case the secondary beam produces a slight reflected ray whose *vis viva* $=\left\{\frac{s-s'}{2+s+s'}\right\}^2 q$, and whose orientation is $-\frac{\pi}{2}$, so that its vibrations, like those of its parent ray, lie in the secondary plane. The orientation (γ_1) of the refracted ray is given by the formula

$$\tan\gamma_1=\frac{2(1+s)}{2+s+s'}\tan\gamma,$$

whence $$\tan\gamma_1-\tan\gamma=\left\{\frac{s-s'}{2+s+s'}\right\}\cdot\tan\gamma.$$

The plane of vibration is therefore rotated in the positive or negative direction, that is, according to our conventions, from left to right, or from right to left according as s is greater or less than s', that is, according as the primary or secondary refracted ray exerts a greater action on the fluid.

The quantity of *vis viva* expended on the fluid is in this case

$$sp_1+s'q_1=\frac{s}{1+s}p+\frac{4s'(1+s)}{(2+s+s')^2}q,$$

which must be employed in working some effect or other upon the fluid.

If we suppose that s and s' are constant for every thin stratum of fluid of the same vertical height $\delta\xi$, since the effect ought to vanish with $\delta\xi$, we may suppose

$$\frac{s-s'}{2+s+s'}=\sigma\delta\xi;$$

and regarding γ as a function of ξ, we have

$$\tan\gamma_1-\tan\gamma=\delta\tan\gamma=\frac{d}{d\xi}\tan\gamma\cdot\delta\xi.$$

Consequently $$\frac{\frac{d}{d\xi}\tan\gamma}{\tan\gamma}=\sigma,$$

whence $$\log.\tan\gamma=\sigma\xi+\log.\tan C, \text{ or}$$
$$\tan\gamma=\tan C.\epsilon^{\sigma\xi}.$$

In this equation C is the initial value of γ at the surface of the fluid, or at the surface of a crystal which possesses the property in question. The circular polarization, as

it is sometimes called, will be right-handed or left-handed according as σ is positive or negative. In the latter case we may put the formula under the shape

$$\cot\gamma = \cot C.\varepsilon^{\sigma i},$$

or

$$\tan\left(\frac{\pi}{2}-\gamma\right) = \tan\left(\frac{\pi}{2}-C\right)\varepsilon^{\sigma i},$$

which shows that for a negative value of σ of equal magnitude, the left-handed spiral will be exactly similar to the right-handed spiral.

Since the nature of the spiral as regards right and left depends on the sign of $s-s'$; when this difference is very small, as it must be when there is no sensible reflected ray (this appears by the value of q'), we see how a very trifling variation of the constitution of the fluid will change the rotation from right to left or from left to right; and this is agreeable to experience; for though the chemist can detect no difference in sugar formed from beetroot and that formed from the cane, yet these are found to possess the property in opposite directions. In the same way the specimens of right-handed and left-handed quartz which possess this property, must owe their difference to the presence of some ingredient, which enters in so minute a proportion as not sensibly to affect either the crystalline form or the chemical composition.

I must say that this successful application of the present theory to the explanation of these singular phenomena, which no one, so far as I am aware, has ever attempted to explain before, gives me great confidence in the truth of the general theory; nor less satisfactory is the perfectly simple and easy manner in which the known laws of refraction, polarization and photometry result from the calculus. I think I may also appeal to the symmetry and elegance of the formulæ themselves, as justifying the inference that they are not less connected with *truth* than with *light*.

37. Several other modes of testing the truth of the present theory have occurred to me, but I have not the time to work them out in detail. Suffice it to say, that hitherto I have not met with a single case with which it seems to be at variance, and I doubt not, whenever the theory of resonance is brought to perfection, that much which is still obscure will be completely explained. The latter theory is at present in a very imperfect state, though the experimental researches of Savart and others have revealed its phenomena with great minuteness of detail, and with a variety of most curious and interesting results. The mathematical difficulties of the subject are such that they will require the highest analytical powers to contend with them; though I cannot hope personally to assist in overcoming them, I am very sanguine that they will finally yield to the intellectual battery of modern analysis, and I am not a little encouraged in this hope by the appearance of M. Lamé's admirable work, 'Leçons sur la Théorie Mathématique de l'Elasticité des Corps Solides,' 8vo. Paris, 1852. Having mentioned the name of M. Lamé, I beg to call attention to the circumstance that his results, as regards the direction of vibration in the polarized ray, coincide with what I have obtained in the present theory, being opposed to those of Fresnel and the more recent researches of M. Cauchy. See "Leçons," &c., p. 132.

38. I return to the subject of reflexion and refraction. In the general theory I have taken the case of a dense refracting medium, as it is usually termed (though I think it will turn out that it should rather be termed a rare refracting medium), in which $\frac{\sin\theta}{\sin\theta_i} > 1$, or $\mu_i > 1$. But all the steps will hold, *mutatis mutandis*, when $\mu_i < 1$, and it may be convenient to exhibit the formulæ adapted to that hypothesis. They are as follows:—

For the primary wave,

$$\frac{h'}{h} = \frac{-\sin(\theta_i - \theta)}{\sin(\theta_i + \theta)}$$

$$\frac{h_i}{h} = \frac{\sin 2\theta}{\sin(\theta_i + \theta)}$$

$$\frac{p'}{p} = \frac{\sin^2(\theta_i - \theta)}{\sin^2(\theta_i + \theta)}$$

$$\frac{p_i}{p} = \frac{1}{1+s} \cdot \frac{\sin 2\theta_i \sin 2\theta}{\sin^2(\theta_i + \theta)}.$$

For the secondary wave,

$$\frac{k'}{k} = \frac{(1+s')\sin 2\theta_i - (1+s)\sin 2\theta}{(1+s')\sin 2\theta_i + (1+s)\sin 2\theta}$$

$$\frac{k_i}{k} = \frac{2(1+s)\sin 2\theta}{(1+s')\sin 2\theta_i + (1+s)\sin 2\theta}$$

$$\frac{q'}{q} = \left\{\frac{(1+s')\sin 2\theta_i - (1+s)\sin 2\theta}{(1+s')\sin 2\theta_i + (1+s)\sin 2\theta}\right\}^2$$

$$\frac{q_i}{q} = \frac{4(1+s)\sin 2\theta_i . \sin 2\theta}{((1+s')\sin 2\theta_i + (1+s)\sin 2\theta)^2}.$$

To which must be added,

$$\sin\theta_i = \frac{1}{\mu_i}\sin\theta = \frac{1+s}{\mu}\sin\theta$$

$$\tan\gamma' = -\tan\gamma \cdot \frac{(1+s')\sin 2\theta_i - (1+s)\sin 2\theta}{(1+s')\sin 2\theta_i + (1+s)\sin 2\theta} \cdot \frac{\sin(\theta_i + \theta)}{\sin(\theta_i - \theta)}$$

$$\tan\gamma_i = \tan\gamma \cdot \frac{2.(1+s).\sin(\theta + \theta_i)}{(1+s_i).\sin 2\theta_i + (1+s)\sin 2\theta}.$$

I have thought it right to give the whole series of formulæ for the convenience of persons who may be possessed of the means to test them experimentally, and I may mention that it is more particularly in the refracted rays that they differ from the formulæ of Fresnel; it is therefore to the latter that I must principally look for the experimental verification of this theory.

It may be as well to write down the formulæ for the secondary wave in case s and s' are equal, or very small when unequal. They are as follows:—

$$\frac{k'}{k} = \frac{\tan(\theta_i - \theta)}{\tan(\theta_i + \theta)}$$

$$\frac{k_i}{k} = \frac{2\sin 2\theta}{\sin 2\theta_i + \sin 2\theta}$$

$$\frac{q'}{q}=\frac{\tan^2(\theta_1-\theta)}{\tan^2(\theta_1+\theta)}$$

$$\frac{q_1}{q}=\frac{4}{1+s}\cdot\frac{\sin 2\theta_1.\sin 2\theta}{(\sin 2\theta_1+\sin 2\theta)^2}$$

$$\tan\gamma'=-\tan\gamma\cdot\frac{\cos(\theta_1+\theta)}{\cos(\theta_1-\theta)}$$

$$\tan\gamma_1=\tan\gamma\cdot\frac{2\sin(\theta_1+\theta)}{\sin 2\theta_1+\sin 2\theta}.$$

For photometrical experiments, it should be remembered that whilst $\frac{p'}{p}$, $\frac{q'}{q}$ express the relative brightness of the *reflected and incident* rays, primary and secondary, $\frac{p_1}{p}$ and $\frac{q_1}{q}$ must be multiplied by $\frac{\cos\theta}{\cos\theta_1}$ to obtain the proper photometrical ratios for the comparison of the *refracted and incident* rays.

39. For the 'critical angle' at which $\sin\theta_1=\frac{\pi}{2}$, we have $\sin\theta=\mu_1$,

$$p'=p,\quad q'=q,$$
$$p_1=0,\quad q_1=0.$$

Both rays are therefore reflected without loss of intensity, and this is true notwithstanding any absorptive tendency of the medium, which in fact the rays do not enter. Compare No. 26 and No. 27.

40. The general value of the polarizing angle for which $q'=0$, will be determined by the equations

$$(1+s)\sin 2\theta=(1+s')\sin 2\theta_1,$$

or
$$(1+s)\sin\theta\cos\theta=(1+s')\sin\theta_1\cos\theta_1,$$

and
$$\sin\theta=\mu_1\sin\theta_1=\frac{\mu}{1+s}\sin\theta_1,$$

whence
$$\cos\theta_1=\frac{1+s}{1+s'}\mu_1\cos\theta=\frac{\mu}{1+s'}\cos\theta.$$

If
$$\mu'=\frac{\mu}{1+s'},$$

we have
$$\cos\theta_1=\mu'\cos\theta$$
$$1-\sin^2\theta_1=\mu'^2(1-\sin^2\theta)$$

or
$$1-\frac{1}{\mu_1^2}\sin^2\theta=\mu'^2-\mu'^2\sin^2\theta,$$

whence
$$\sin^2\theta=\frac{(1-\mu'^2)\mu_1^2}{1-\mu_1^2\mu'^2}$$

$$\cos^2\theta=\frac{1-\mu_1^2}{1-\mu_1^2\mu'^2}$$

$$\tan^2\theta=\frac{(1-\mu'^2)\mu_1^2}{1-\mu_1^2}$$

$$\tan\theta=\mu_1\sqrt{\frac{1-\mu'^2}{1-\mu_1^2}}.$$

When μ_i is >1, as in the case of dense refracting substances, glass, water, &c., the better form for the polarizing angle is

$$\tan\theta=\mu_i\sqrt{\frac{\mu'^2-1}{\mu_i^2-1}}.$$

41. If there be no absorption, $\mu=\mu_i=\mu'$,

and $\tan\theta=\mu$.

If the primary and secondary rays are equally absorbed,

$$\mu'=\mu_i \text{ and } \tan\theta=\mu_i.$$

42. In the theory of the primary wave, whose vibrations are performed in the plane of incidence, although I have supposed that these vibrations are perpendicular to the directions of the incident, reflected and refracted rays, yet the same demonstration will hold whatever be the inclination of the vibrations to the rays, provided it be the same for all the three rays. If we denote by ε this constant angle of vibration, the only change necessary to be made in the wording of No. 14. is, for "transverse" to read *oblique*, and instead of the words "each turned from right to left through a right angle," to read *each turned from right to left through an angle* (ε). Hence, whatever be the value of ε, the intensity of the reflected ray will be properly represented by $\frac{\sin^2(\theta-\theta_i)}{\sin^2(\theta+\theta_i)}$. If $\varepsilon=0$, the vibrations are longitudinal, as in the case of sound.

If $\varepsilon=0$, we have exactly the case which has been treated by Mr. Green*; as is manifest from his *symbols*; though his language is indefinite as regards the direction of vibration.

It is therefore extremely interesting to compare Mr. Green's expression for the intensity of the reflected ray, or rather the square of his expression (for he seems to use the word intensity in a different sense, namely, that of comparative velocity), with the expression $\frac{\sin^2(\theta-\theta_i)}{\sin^2(\theta+\theta_i)}$, observing beforehand, that, from the way in which he has simplified the calculus, we ought to expect nothing more than an approximate coincidence. The square of Mr. Green's expression is $\frac{\left(\frac{\varrho_i}{\varrho}-\frac{\cot\theta_i}{\cot\theta}\right)^2}{\left(\frac{\varrho_i}{\varrho}+\frac{\cot\theta_i}{\cot\theta}\right)^2}$. In applying his formula to the case of two gases of different densities, whose constitution admits of their remaining in juxtaposition under the same pressure, he in the first place deduces the equation

$$\frac{\varrho_i}{\varrho}=\frac{\sin^2\theta}{\sin^2\theta_i}$$

from the known experimental relations between the pressure and the expansion of such gases, combined with other parts of his theory; and this substitution being made, the square of his formula becomes $\frac{\tan^2(\theta-\theta_i)}{\tan^2(\theta+\theta_i)}$, which, singularly enough, coincides with

* Cambridge Transactions, vol. vi. p. 403.

FRESNEL's expression for a ray polarized perpendicularly to the plane of incidence, that is, according to FRESNEL's views, whose vibrations are performed in the plane of incidence, a result which, at first sight, seems to militate against the expression I have obtained for the case under consideration, viz. $\frac{\sin^2(\theta-\theta_1)}{\sin^2(\theta+\theta_1)}$. But I beg to observe, that the juxtaposition of two heterogeneous gases of different densities under a constant pressure is not at all analogous to the case of light as conceived in the present communication. For, instead of heterogeneous fluids under a constant pressure, we have to conceive pure ether of one density in contact with pure ether of a different density, and therefore under a different pressure, such difference of density and pressure being due to the attractions or repulsions of the grosser particles of the medium for the particles of the ether. We have therefore no right to make the substitution $\frac{\varrho_1}{\varrho}=\frac{\sin^2\theta}{\sin^2\theta'}$, the truth of which rests entirely on a property peculiar to gases.

It is much more natural to suppose that the density of the ether in the interior of crystals does not differ much from that of the surrounding ether, so that the ratio $\frac{\varrho_1}{\varrho}$ does not sensibly differ from unity. Replacing this ratio by unity, Mr. GREEN's expression becomes

$$\frac{1-\frac{\cot\theta_1}{\cot\theta}}{1+\frac{\cot\theta_1}{\cot\theta}}=\frac{\tan\theta_1-\tan\theta}{\tan\theta_1+\tan\theta}=-\frac{\sin(\theta-\theta_1)}{\sin(\theta+\theta_1)},$$

the square of which gives $\frac{\sin^2(\theta-\theta_1)}{\sin^2(\theta+\theta_1)}$ for the intensity of the reflected ray, agreeably to the present theory. This curious interchange of the expressions $\frac{\sin^2(\theta-\theta_1)}{\sin^2(\theta+\theta_1)}$ and $\frac{\tan^2(\theta-\theta_1)}{\tan^2(\theta+\theta_1)}$, according to the different circumstances of the case, is very remarkable, and tends to throw light on the discrepancies of different theorists, as regards the direction of vibration.

It is further remarkable that a similar interchange, according as we substitute $\frac{\sin^2\theta}{\sin^2\theta_1}$, or 1 for the ratio $\frac{\varrho_1}{\varrho}$, occurs in the expression for the change of phase, as investigated by Mr. GREEN, in the case of total reflexion at an angle greater than the critical angle. In fact, if $2e$ denote the acceleration of phase in the reflected ray, the following general formula will be found to result from Mr. GREEN's equations,

$$\tan e=\frac{\varrho}{\varrho_1}\sqrt{\tan^2\theta-\mu^2\sec^2\theta},$$

which transforms itself into $\tan e=\frac{1}{\mu\cos\theta}\sqrt{\frac{\sin^2\theta}{\mu^2}-1}$,

or into $$\tan e = \frac{\mu}{\cos\theta}\sqrt{\frac{\sin^2\theta}{\mu} - 1},$$

according as μ^2 or 1 is substituted in the place of $\frac{\varrho_1}{\varrho}$.

The former is the expression which Mr. GREEN has obtained for contiguous gases, and is identical with that obtained by FRESNEL by an interpretation of the formula $\frac{\tan(\theta_1-\theta)}{\tan(\theta_1+\theta)}$; the latter is identical with that obtained by FRESNEL from the formula $\frac{\sin(\theta_1-\theta)}{\sin(\theta_1+\theta)}$. According to the views of the present author, the latter will belong to a totally reflected ray whose vibrations are performed in the plane of incidence, and the former to a similar ray whose vibrations are at right angles to that plane.—*This and the preceding paragraph were added April* 2, 1854.

III. *On some of the Products of the Decomposition of Nitrotoluylic Acid.*

By Henry M. Noad, *Ph.D., Lecturer on Chemistry at St. George's Hospital.*

Received November 17,—Read December 8, 1853.

In a paper read before the Chemical Society, and published in the third volume, p. 421, of the Transactions of that body, I described the mode of preparation and properties of two new organic acids, which, from their general analogy to benzoic and nitro-benzoic acids, were considered to be the representatives of those acids in the succeeding or *Toluyl* series, and were named accordingly *Toluylic* ($C_{16}H_8O_4$) and Nitrotoluylic $\left(C_{16}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}O_4\right)$ acids.

These two acids, interesting as supplying two members of a well-defined series of acids, and as establishing a parallelism between the benzoyl and toluyl groups, were formed by the oxidation of *Cymol*, a hydrocarbon ($C_{20}H_{14}$) occurring with *cuminol*, an oxyhydrocarbon ($Cl_{20}H_{12}O_2$) in the oil of cumin (*Oleum cumini*), from which source alone they have hitherto been obtained.

The original object in submitting cymol to the action of fuming nitric acid was the formation of the substitution compound $C_{20}\left\{\begin{matrix}H_{13}\\NO_4\end{matrix}\right\}$, from which, by the action of reducing agents, it was anticipated that an organic base, analogous to those formed from nitrobenzole (aniline)*, from nitrotoluole (toluidine)†, and from nitrocumole (cumidine)‡, would have been obtained: the unexpected formation however of a crystalline acid gave a different turn to the investigation, and the search for cimidine ($C_{20}H_{13}N$) was for the time laid aside.

I have at various times since the publication of this first paper returned to the study of the action of nitric acid on cymol, and have made many attempts, by employing acids of various degrees of strength, by keeping down the temperature by surrounding the vessels with freezing mixtures, &c., to check the action of the acid before it had produced its maximum degree of oxidation on the oil; yet though I have in this way obtained several beautifully crystallized intermediate products, and amongst them a compound homologous to *dinitrobenzole*, in which two equivalents of the hydrogen of the oil have given place to two of hyponitric acid, viz. $C_{20}\left\{\begin{matrix}H_{12}\\2NO_4\end{matrix}\right\}$, still the principal

* Zinin, Annal. der Chem. und Pharm. Bd. xliv, p. 283.

† Muspratt and Hofmann, Mem. Chem. Soc. vol. ii. p. 373.

‡ Nicholson, Chem. Soc. Quart. Journ. vol. i. p. 2.

product of the action has been nitrotoluylic acid; and I have not hitherto succeeded in obtaining the first substitution compound $C_{20}\left\{\begin{matrix}H_{19}\\NO_4\end{matrix}\right\}$, and of the intermediate substances above alluded to, quantities insufficient for a thorough investigation of their nature.

The study of the products of the decomposition of nitrotoluylic acid has been attended with more successful results: some new and interesting compounds have been obtained, and as these, viewed in connection with those described in my former paper, and with those of CHANCEL obtained in his researches on nitrobenzoic acid*, complete the proofs of the parallelism of the benzoyl and toluyl groups, I have thought that a brief account of them might be deemed not unworthy of the notice of the Royal Society.

Preparation of Nitrotoluylamide.

Among the salts analysed in order to determine the atomic weight of nitrotoluylic acid was the ethyl compound, prepared by submitting an alcoholic solution of the acid to a current of dry hydrochloric acid gas till copious fumes were evolved, and then distilling. Some attempts were made to convert this ether into nitrotoluylamide by saturating its alcoholic solution with dry ammoniacal gas, and setting it aside in a well-stopped bottle; after some months however the anticipated transformation had not taken place. Equally unsuccessful was the attempt to prepare this amide by the action of heat on nitrotoluylate of ammonia, as FIELD† procured *cuminamide* from cuminate of ammonia; an explosion invariably took place, however carefully the heat was applied. This investigation was resumed by repeating the experiment with the ether in sealed tubes exposed to heat in a water-bath. About 5 grms. of the crystallized salt were placed in a stout glass tube, 2 feet long and three quarters of an inch in diameter; the tube was then filled to within 2 inches of the top with strong aqueous ammonia, sealed, and submitted to a boiling temperature in a deep water-bath. After forty-eight hours' continuous action the upper part of the tube had become filled with brilliant yellow crystalline plates, which were easily removed on breaking the tube from the solid and unaltered ether below. Two or three crystallizations sufficed for their purification. They were dried *in vacuo* over sulphuric acid, and then slowly brought to their fusing-point in the air-bath. The crystals began to fuse at 245° FAHR.; at 255° they were fairly liquid, and at 260° they emitted copious vapours.

Analysis.—The combustion was made in the usual manner with oxide of copper:

I. ·524 grm. yielded 1·029 grm. carbonic acid and ·220 grm. water.

II. ·420 grm. gave ·886 grm. carbonic acid and ·187 grm. water.

* Compt. Rend. vol. xxviii. p. 293; LAURENT and GERHARDT, C. R. 1849, p. 177; Journ. Pr. Chem. xlvii. p. 140; Ann. Ch. Pharm. lxxii. 274.

† Mem. Chem. Soc. vol. iii. p. 404.

These numbers furnish the following per-centages of carbon and hydrogen:—

	I.	II.
Carbon	53·55	53·69
Hydrogen	4·66	4·61

The formula of nitrotoluylamide, $C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_2, NH_2$, or if we adopt the theory of KOLBE, that toluylic acid like benzoic acid is the oxide of a conjugate radical $(C_{14}H_7)\frown C^2$

$$\left(C_{14}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}\right)\frown C^2\left\{\begin{matrix}O_2\\NH_2\end{matrix}\right.$$

requires

Carbon	53·33
Hydrogen	4·44

Properties.—Nitrotoluylamide is in its properties exactly analogous to nitrobenzamide, from which it differs in composition by (C_2H_2), the constant ascending or descending term of these organic series. It is very sparingly soluble in cold water, more so in hot; but very soluble in alcohol, ether, and pyroxylic spirit. Its alcoholic solution crystallizes spontaneously in long, brilliant, yellow needles. Its fusing-point is about 245° FAHR.; that of *nitrobenzamide* was determined by CHANCEL to be under 212°; when heated with a concentrated solution of potash, it is converted into nitrotoluylate of that base.

By the process above described for procuring this substance, it can only be obtained in very limited quantities, and the process is by no means unattended with danger, from the liability of the tube to burst under the great pressure to which it is exposed; and whilst searching for some better method of procuring it in quantities sufficient to study the products of its decomposition, I became acquainted with the investigations of CHANCEL upon the nitro-compounds derived from benzoic acid*, and upon trying the method there proposed by him for the preparation of nitrobenzamide, I succeeded, after many fruitless trials, in obtaining the new amide in considerable quantities. The purified ethyl compound was dissolved in ordinary spirits of wine, and aqueous ammonia added until a precipitate began to form: the solution was transferred to a stout green glass bottle, and the stopper being well-secured, it was plunged into a water-bath and kept for several days at a temperature of about 140° FAHR. The action proceeded very slowly; with about 15 grammes of ether it was usually completed in eight or ten days. The liquid, from being nearly colourless, was now of a deep yellow colour, and no precipitation took place on the addition of a large quantity of water. The ammoniacal alcohol was distilled off, and the residual crystalline mass redissolved in weak alcohol and boiled with animal charcoal; from the filtered solution pure nitrotoluylamide separated in crystals of remarkable size and brilliancy.

The formation of nitrotoluylamide by the action of ammonia on nitrotoluylate of

* LAURENT and GERHARDT, C. R., 1849, 177, Annual Rep. Prog. Chem. vol. iii. part 1. p. 223.

oxide of ethyl is represented in the following equation:—

$$C_4H_5O, C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_2+NH_3=C_4H_5O, HO,+C_{16}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_2, NH_3.$$

Action of Reducing Agents on Nitrotoluylamide.

When an alcoholic solution of nitrotoluylamide is submitted to the action of hydrosulphate of ammonia, the reaction is of a complicated nature, the alcohol itself undergoes decomposition, and its elements take a part in the formation of the new products. But an aqueous solution of the amide undergoes under the influence of this reducing agent a very interesting decomposition, precisely analogous to that of nitrobenzamide under similar circumstances. Ten grammes of the substance were dissolved in three pints of boiling distilled water, and agitated while still hot with strong solution of hydrosulphate of ammonia; the liquid was then thoroughly saturated with sulphuretted hydrogen, the bottle well stopped, and kept for several days plunged in a water-bath at the temperature of about 140° Fahr. The solution, which had now acquired a dark brown colour, was slowly evaporated on the water-bath; large quantities of sulphur separated during the evaporation, which were from time to time removed. When the liquid was reduced to about six ounces it was filtered and set aside. In a few hours a mass of fawn-coloured crystals was deposited; these were redissolved in water and boiled twice with animal charcoal. On cooling, a crop of beautiful pale-yellow cubical crystals made their appearance; these were again digested with animal charcoal, and from the filtered solution, fine, large, nearly colourless and transparent rhombic prisms of the new substance were obtained. They were dried first between folds of bibulous paper, and then *in vacuo* over sulphuric acid, after which no further diminution in weight took place on reducing them to powder and heating them for two hours in an air-bath at their melting-point, viz. 240° Fahr. Unlike therefore the homologous compound obtained by Chancel from nitrobenzamide, this substance contains no water of crystallization. When the fused mass was removed from the air-bath, at the moment of solidification, it burst with a slight explosion into a heap of glistening crystalline plates.

Analysis.—The combustion was made in the usual manner with oxide of copper.

I. ·442 grm. produced 1·035 grm. carbonic acid and ·270 grm. water.

II. ·4057 grm. yielded ·948 grm. carbonic acid and ·249 grm. water,

numbers which correspond centesimally to

	I.	II.
Carbon	63·86	63·72
Hydrogen . . .	6·79	6·82

On heating a portion of the substance with soda-lime in a green glass retort, ammonia was first plentifully disengaged; but on raising the heat a yellowish oily liquid distilled over, which in the course of half an hour solidified into a crystalline mass, having the peculiar smell of the *aniline* class of organic bases. Although no doubt was entertained that this substance was *toluidine*, it was thought desirable to deter-

mine the fact experimentally. Three or four grammes of the new substance were therefore distilled with caustic potash, and the solid product, after having been washed two or three times with water, was saturated with an alcoholic solution of oxalic acid. It was evaporated to dryness on the water-bath, then redissolved in boiling alcohol and filtered; the crystals which separated on cooling were washed with cold distilled water, then redissolved in boiling water, and decomposed by caustic potash; some clear oily drops separated, which were dissolved in ether, and the etherial solution evaporated to dryness. The residue was dissolved in hydrochloric acid, and mixed with an alcoholic solution of bichloride of platinum; a fine orange-coloured crystalline mass was obtained, which was washed with ether and dried on the water-bath. It was decomposed by ignition in a porcelain crucible.

Analysis.—·595 grm. yielded ·1872 grm. of metallic platinum = 31·46 per cent. The formula of the double chloride of platinum and toluidine ($C_{14}H_9N$, HCl, $PtCl_2$) requires 31·6 per cent. of platinum.

The crystalline body obtained by the distillation of the new substance with caustic potash was therefore evidently *toluidine*.

The decomposition which nitrotoluylamide undergoes under the influence of hydrosulphate of ammonia is in exact accordance with the reactions constantly observed between this reducing agent and nitrated organic bodies, and is represented in the following equation:—

$$C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_2, NH_2+6HS=C_{16}H_{10}N_2O_2+4HO+6S.$$

Nitrotoluylamide. New substance.

The proportion per cent. of carbon and hydrogen required by the formula

$$C_{16}H_{10}N_2O_2$$

are,

Carbon	64·00
Hydrogen	6·61

which agree very closely with those obtained by the combustion of the new substance with oxide of copper.

This substance has two homologues in the benzoyl or immediately preceding series, viz. *carbamide—carbanilide*, a neutral body discovered by Dr. Hofmann*, and the true *urea* of the aniline series discovered by M. Chancel†, both represented by the formula

$$C_{14}H_8N_2O_2=C_{16}H_{10}N_2O_2-C_2H_2.$$

The origin of the crystalline compound under examination, which is perfectly analogous to that of *aniline urea*, renders it at once probable that it is the analogue of the latter, an assumption which was fully corroborated by the study of its properties and chemical deportment.

* Chem. Soc. Quart. Journ. vol. ii. p. 36.

† Compt. Rend. xxviii. p. 293; Laurent and Gerhardt, C. R. 1849, p. 177; Journ. Pr. Chem. xlvii. p. 140; Ann. Ch. Pharm. lxxii. p. 274.

It has all the chemical functions of ordinary urea, its taste is cooling and slightly bitter; it is very soluble in water, alcohol, and ether. Its aqueous solution may be kept for some time without change, but after some weeks it acquires a brownish colour, and flocculent matter is deposited. It is a true organic base, and forms crystalline compounds with several acids. On dissolving some of the crystals in weak nitric acid and placing the solution under a bell jar over sulphuric acid, the whole soon became a crystalline mass; and when the small quantity of adhering nitric acid was removed by affusion with cold water, and the crystals dissolved and boiled with animal charcoal, the nitrate was obtained by spontaneous evaporation in large and nearly colourless thin plates, the taste of which was cooling and slightly bitter, hardly to be distinguished from that of nitre. By dissolving some of the crystals in dilute oxalic acid, and placing the filtered solution over sulphuric acid, a crystalline mass was obtained, from which the oxalate of the new base was obtained in long, transparent, and nearly colourless needles, by washing away as before the excess of acid, redissolving in water, and allowing the solution to crystallize spontaneously. The limited quantity of this substance at my disposal, and the very great difficulty of preparing it, prevented my making a quantitative determination of any of its salts. When heated a little above its fusing-point the base takes fire, burning with a red smoky flame and leaving much carbon. I propose for it the name of *toluyl-urea*; its relation with Chancel's compound and with the urea type appears from the following synopsis:—

Urea	$C_2 H_4 N_2 O_2$
Anilo-urea . .	$C_2 H_3 (C_{12} H_5) N_2 O_2$
Toluyl-urea . .	$C_2 H_3 (C_{14} H_7) N_2 O_2$.

Product of the Decomposition of Toluyl-urea.

On heating some of the pulverized crystals strongly with caustic potash, ammonia was first disengaged, and then *toluidine* distilled over; when, however, an aqueous solution was boiled with a solution of caustic potash till ammonia ceased to be evolved and the potash then neutralized with an acid, the acid being left slightly in excess, a clear yellow liquid was obtained, from which after a few hours' standing there was deposited a group of magnificent golden-yellow needles, which only required a second solution and crystallization to render them perfectly pure. They were dried first between folds of filtering paper, then reduced to powder and thoroughly dried in the air-bath, after which they underwent no further loss of weight by being fused.

Analysis.—This was made in the ordinary manner by combustion with oxide of copper.

I. ·3355 grm. produced ·780 grm. carbonic acid and ·188 grm. water.

II. ·4042 grm. gave ·939 grm. carbonic acid and ·224 grm. water,

corresponding centesimally to

	I.	II.
Carbon	63·46	63·22
Hydrogen	6·22	6·15

By heating with soda-lime toluidine distilled over and solidified in the receiver. The new body thus formed is a well-defined acid, producing a series of crystalline salts; those of potash, soda, and ammonia, crystallized with difficulty; the lime and baryta salts, though exceedingly soluble, were obtained after long standing over sulphuric acid in fine acicular tufts. The lead salt was obtained by dropping the ammonia compound into solution of acetate of lead; it fell as a white powder, which when boiled with a large quantity of distilled water, and filtered, separated, as the solution cooled, in the form of long, brilliant, transparent, and nearly colourless needles with tufted ends. By decomposing this lead salt by dilute sulphuric acid, the new acid was again obtained in long needles having a fine crimson colour. On adding a solution of the ammonia salt to a solution of nitrate of silver, a copious gray crystalline precipitate fell, which, when washed with cold distilled water, and then redissolved in a large quantity of boiling water, furnished the silver salt of the new acid in the form of thin plates, of a glistening and brilliant appearance. After a second crystallization the salt was dried in the dark *in vacuo* over sulphuric acid, and then submitted to analysis.

Analysis.—I. ·495 grm. gave ·672 grm. carbonic acid and ·148 grm. water.

II. ·318 grm. left by ignition in a porcelain capsule ·132 grm. of metallic silver.

III. ·337 grm. left ·1409 grm. of silver,

results which correspond in 100 parts to

	I.	II.	III.
Carbon	37·02		
Hydrogen. . . .	3·32		
Silver		41·51	41·81.

If we assume that this new acid is formed from toluyl-urea by the elimination of one equivalent of ammonia and by the assumption of the elements of two equivalents of water, the substance thus hypothetically obtained will be represented by the formula

$$C_{16}H_9NO_4;$$

thus

$$\begin{array}{l} C_{16}H_{10}N_2O_2 \\ -H_3N \\ \hline C_{16}H_7NO_2 \\ +H_2O_2 \\ \hline C_{16}H_9NO_4 \end{array}$$

and on comparing the numbers obtained by the analysis of the acid and its silver salt with those calculated from the above formula, we find such an agreement as to place beyond doubt the accuracy of the assumption.

Thus, the formula

$$C_{16}H_9NO_4$$

requires

Carbon	63·57
Hydrogen	5·95

and that of AgO, $C_{16}H_8NO_3$, requires

Carbon	37·21
Hydrogen	3·10
Silver	41·86

The numbers actually obtained from the analysis of the acid and its silver salt are, for the acid,—

Mean.

Carbon	63·34
Hydrogen	6·18

for the silver salt,—

Carbon	37·02
Hydrogen	3·32
Silver	41·66

This acid, for which I propose the provisional name of *Carbo-toluylic acid*, has several representatives in the *benzoyl* series, viz. *anthranilic acid*, obtained by Fritzsche by the action of caustic potash on indigo; *benzamic acid*, the product of the action of hydrosulphuric acid on nitrobenzoic acid discovered by Zinin; and, lastly, *carbanilic acid*, prepared by Chancel, by treating nitrobenzamide with hydrosulphuric acid. Of these three acids, which are all represented by the formula

$$C_{14}H_7NO_4=C_{16}H_9NO_4-C_2H_2,$$

benzamic and *carbanilic* acids have lately been found by M. Gerland* to be identical, while *anthranilic* acid is a body of a different type. It remains to be examined, to which of these two acids, whether to *anthranilic* or to *carbanilic* acids, the new acid above described corresponds. The mode of its generation would render it probable that it is homologous to *carbanilic* acid, whence the provisional name I have assigned to it; should it however prove on further examination to correspond rather to *anthranilic* acid, then the convertibility of this acid into *salicylic* acid by means of nitrous acid, first suggested by Dr. Hofmann†, and lately experimentally confirmed by M. Gerland‡, would appear to indicate that the analogous transformation of the new acid would furnish a series of new substances which at present are entirely wanting, namely, the proper homologues of salicylic acid and its derivatives. Thus:—

$$\underset{\text{Anthranilic acid.}}{HO, C_{14}H_6NO_3}+NO_3=\underset{\text{Salicylic acid.}}{HO, C_{14}H_5O_3}+2N+HO$$

$$\underset{\text{New acid.}}{HO, C_{16}H_8NO_3}+NO_3=\underset{\text{Homologue of salicylic acid.}}{HO, C_{16}H_7O_3}+2N+HO$$

The extreme difficulty however of preparing the different substances described in

* Quart. Journ. Chem. Soc. vol. v. p. 133. † Ibid. vol. iii. p. 235. ‡ Ibid. vol. v. p. 133.

this paper, and more especially the costly nature of the hydrocarbon (cymol), which constitutes the (at present) only known source of the parent acid, viz. nitrotoluylic acid, form unfortunate barriers to the continuation of the investigation. *Cymol*, however, doubtless exists among the liquid products of the distillation of coal; indeed, Mr. MANSFIELD, in his valuable memoir on Coal Tar*, describes a fluid which distils over between 170° and 172° (338° to 342° FAHR.), "which bears so strong a resemblance to cymol in odour, and in other properties, as to induce a belief that this body is identical with the hydrocarbon existing in cumin oil." It is my intention to search for it in this fluid, and should it prove possible to obtain it cheaply and in abundance, the experiment above suggested, and many others of equal scientific interest, will be made, the results of which I shall hope to be allowed the honour of submitting to the Royal Society.

In conclusion, I will give a tabular view of the corresponding members of the benzoyl and toluyl groups, the parallelism of which in the present and previous memoir I have had the pleasure of establishing.

Benzoyl series.	Toluyl series.
$\underbrace{HO, C_{14}H_5O_3}$	$\underbrace{HO, C_{16}H_7O_3}$
Benzoic acid.	Toluylic acid.
$\underbrace{HO, C_{14}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_3}$	$\underbrace{HO, C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_3}$
Nitrobenzoic acid.	Nitrotoluylic acid.
$\underbrace{C_{14}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_2, NH_2}$	$\underbrace{C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_2, NH_2}$
Nitrobenzamide.	Nitrotoluylamide.
$\underbrace{C_2H_3(C_{12}H_5)N_2O_2}$	$\underbrace{C_2H_3(C_{14}H_7)N_2O_2}$
Anilo-urea.	Toluyl-urea.
$\underbrace{HO, C_{14}H_6NO_3}$	$\underbrace{HO, C_{16}H_8NO_3}$
Carbanilic acid.	Carbo-toluylic acid.

* Chem. Soc. Quart. Journ. vol. i. p. 244.

IV. *Researches on the Geometrical Properties of Elliptic Integrals.*

By the Rev. JAMES BOOTH, *LL.D., F.R.S. &c.*

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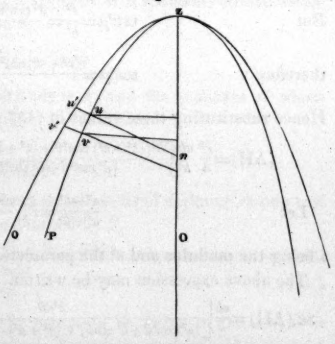
SECTION XI.—*On the Quadrature of the Logarithmic Ellipse and of the Logarithmic Hyperbola.*

LXXXIV. IN the former part of this paper, printed in the Philosophical Transactions for the year 1852, the author has shown that the geometrical types of those integrals, named by LEGENDRE and others elliptic functions, are the curves of symmetrical intersection of surfaces of the second order. In the progress of those investigations he discovered two curves, which he called the *Logarithmic Ellipse* and the *Logarithmic Hyperbola*. The properties of these curves have the same analogy to the paraboloid of revolution that spherical conics have to a sphere, or which ordinary conic sections bear to a plane. To determine the areas of those curves, or rather the portions of surface of the paraboloid bounded by them, appeared to the author a problem not undeserving of investigation.

Fig. 27.



The logarithmic ellipse is defined as the curve of intersection of a paraboloid of revolution with an elliptic cylinder whose axis coincides with that of the paraboloid.

The logarithmic hyperbola, in like manner, may be defined as the curve of intersection of a paraboloid of revolution with a cylinder whose base is an hyperbola, and whose axis coincides with that of the paraboloid.

Through the vertex Z of the paraboloid let two parabolas be drawn indefinitely near to each other, ZP, ZQ, and let two planes indefinitely near to each other at right angles to the axis OZ cut the parabolas in the points u, u', v, v'.

The little trapezoid $uvu'v'$ is the element of the surface, and if the normal un makes the angle μ with the axis OZ, $d\psi$ being the elementary angle between the planes, $uu'=k\tan\mu d\psi$, k being the semiparameter of the generating parabola.

Now $uv=ds=k\frac{d\mu}{\cos^3\mu}$. Hence the elementary trapezoid $uvu'v'=\frac{k^3\sin\mu d\mu d\psi}{\cos^4\mu}$.

Integrating this expression, area $=k^3\int d\psi\int\frac{\sin\mu}{\cos^4\mu}d\mu$; . . . . . (436.)

or performing the integration with respect to μ,

$$\text{area}=\frac{k^2}{3}\int d\psi \sec^3\mu + \text{constant}.$$

Now when the area is 0, sec $\mu=1$, and therefore

$$\text{constant}=-\frac{k^2}{3}\int d\psi. \quad \text{Whence}$$

$$\text{area}=\frac{k^2}{3}\int d\psi(\sec^3\mu-1). \qquad (437.)$$

This is the general expression for the surface of a paraboloid between two principal planes, and bounded by a curve.

When this curve is the logarithmic ellipse, let the area be put (ΔH).

We must now express ψ and μ as functions of another variable θ.

Let $x=a\cos\theta$, $y=b\sin\theta$; the base of the cylinder being the ellipse whose equation is $\frac{x^2}{a^2}+\frac{y^2}{b^2}=1$. ψ is the angle which $\sqrt{x^2+y^2}$ makes with the axis a.

Now
$$\tan\psi=\frac{y}{x}=\frac{b}{a}\tan\theta, \qquad (438.)$$

and
$$d\psi=\frac{ab\,d\theta}{a^2\cos^2\theta+b^2\sin^2\theta}. \qquad (439.)$$

But
$$\tan^2\mu=\frac{r^2}{k^2}=\frac{a^2\cos^2\theta+b^2\sin^2\theta}{k^2};$$

therefore
$$\sec^2\mu=\frac{(k^2+a^2)\cos^2\theta+(k^2+b^2)\sin^2\theta}{k^2}. \qquad (440.)$$

Hence substituting these values in (437.), we get for the area

$$(\Delta\text{H})=\frac{k^2}{3}\frac{ab}{k^3}\int\frac{d\theta[(k^2+a^2)\cos^2\theta+(k^2+b^2)\sin^2\theta]^{\frac{3}{2}}}{[a^2\cos^2\theta+b^2\sin^2\theta]}-\frac{k^2}{3}ab\int\frac{d\theta}{a^2\cos^2\theta+b^2\sin^2\theta}. \qquad (441.)$$

Let
$$\frac{a^2-b^2}{a^2+k^2}=i^2, \quad \frac{a^2-b^2}{a^2}=e^2, \qquad (442.)$$

i being the modulus and e^2 the parameter, as in (15.).

The above expression may be written

$$\left.\begin{aligned} 3d.(\Delta\text{H})=&\frac{ab}{k}\left[\frac{k^4 d\theta}{(a^2\cos^2\theta+b^2\sin\theta)\sqrt{(k^2+a^2)-(a^2-b^2)\sin^2\theta}}\right]\\ &+\frac{2ab}{k}\frac{k^2 d\theta}{\sqrt{(k^2+a^2)-(a^2-b^2)\sin^2\theta}}\\ &+\frac{ab}{k}\frac{(a^2\cos^2\theta+b^2\sin^2\theta)}{\sqrt{(k^2+a^2)-(a^2-b^2)\sin^2\theta}}\\ &-k^3\frac{d\left(\frac{b}{a}\tan\theta\right)}{1+\left(\frac{b^2}{a}\tan\theta\right)^2} \end{aligned}\right\} \qquad (443.)$$

Therefore, integrating the preceding expression,

$$\left.\begin{aligned} 3(\Delta H)=&\frac{bk^3}{a\sqrt{k^2+a^2}}\int\frac{d\theta}{[1-e^2\sin^2\theta]\sqrt{1-i^2\sin^2\theta}}\\ &-\frac{2abk}{\sqrt{k^2+a^2}}\int\frac{d\theta}{\sqrt{1-i^2\sin^2\theta}}\\ &+\frac{ab}{k}\sqrt{a^2+k^2}\int d\theta\sqrt{1-i^2\sin^2\theta}-k^3\tan^{-1}\left(\frac{b}{a}\tan\theta\right)\end{aligned}\right\}\quad\ldots\ldots\quad(444.)$$

Hence the area of the logarithmic ellipse, or rather the area of the paraboloid bounded by the logarithmic ellipse, may be expressed as a sum of elliptic integrals of the first, second and third orders, with a circular arc.

Since $\frac{a^2-b^2}{a^2}>\frac{a^2-b^2}{a^2+k^2}$, $e^2>i^2$, or the function of the third order is of the circular form.

Assume a spherical conic section such that

$$\tan\alpha=\frac{a}{k},\quad \tan\beta=\frac{b}{k},\quad i^2=\frac{a^2-b^2}{a^2+k^2},$$

therefore $$\frac{\tan\beta}{\tan\alpha}\cos\alpha=\frac{bk}{a\sqrt{a^2+k^2}},\quad \sin^2\varepsilon=\frac{a^2-b^2}{a^2+k^2},\quad e^2=\frac{a^2-b^2}{a^2}.$$

Combining the first and last terms of the preceding equation, they become

$$-k^3\left[\tan^{-1}\left(\frac{b}{a}\tan\theta\right)-\frac{\tan\beta}{\tan\alpha}\cos\alpha\int\frac{d\theta}{[1-e^2\sin^2\theta]\sqrt{1-\sin^2\varepsilon\sin^2\theta}}\right].$$

Now this is the expression for the surface of a segment of a spherical ellipse whose principal angles are 2α and 2β*. Let this be S.

In the next place, $$k\sqrt{a^2+k^2}\int d\theta\sqrt{1-i^2\sin^2\theta}$$

is a portion of the elliptic cylinder whose altitude is k, and the semiaxes of whose base are $\sqrt{a^2+k^2}$ and $\sqrt{b^2+k^2}$. Let this be E,

and $$\frac{abk}{\sqrt{a^2+k^2}}\int\frac{d\theta}{\sqrt{1-i^2\sin^2\theta}}$$

is an expression for an arc of the spherical parabola whose focal distance is one-half the focal distance of the former. Let this be denoted by P.

Hence if we denote the entire surface round Z by $[\Delta H]$,

$$3[\Delta H]=4k\mathrm{E}+\frac{8abk}{\sqrt{b^2+k^2}}\mathrm{P}-4k^2\mathrm{S}.\quad\ldots\ldots\quad(445.)$$

Or the area of the logarithmic ellipse may be expressed as a sum of the arcs of a plane ellipse, of a spherical ellipse, and of a spherical parabola, multiplied by constant linear coefficients.

LXXXV. To find the area of the logarithmic hyperbola.

The general expression for the area, as in (437.), is $\frac{k^2}{3}\int(\sec^3\mu-1)d\psi$.

* See the Theory of Elliptic Integrals, and the Properties of Surfaces of the Second Order, applied to the investigation of the motion of a body round a fixed point, p. 16.

Now the equation of the base of the hyperbolic cylinder being $\frac{x^2}{a^2}-\frac{y^2}{b^2}=1$,

let $$x=a\sec\theta,\ y=b\tan\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (446.)$$

then $$\tan\psi=\frac{y}{x}=\frac{b}{a}\sin\theta,$$

and $$\frac{d\psi}{\cos^2\psi}=\frac{b}{a}\cos\theta d\theta,\ \cos^3\psi=\frac{a^2}{a^2+b^2\sin^2\theta};$$

hence $$d\psi=\frac{ab\cos\theta d\theta}{a^2+b^2\sin^2\theta}.$$

Since $$\tan^2\mu=\frac{r^2}{k^2}=\frac{a^2+b^2\sin^2\theta}{k^2\cos^2\theta},$$

$$\sec^2\mu=\frac{a^2+k^2\cos^2\theta+b^2\sin^2\theta}{k^2\cos^2\theta};$$

$$\therefore\quad \sec^3\mu=\frac{[k^2\cos^2\theta+a^2+b^2\sin^2\theta]^{\frac{3}{2}}}{k^3\cos^3\theta}.$$

Let $(A\Upsilon)$ denote the area of the logarithmic hyperbola, then

$$3(A\Upsilon)=k^3\int\frac{[k^2\cos^2\theta+a^2+b^2\sin^2\theta]^{\frac{3}{2}}ab\cos\theta d\theta}{k^3\cos^3\theta[a^2+b^2\sin^2\theta]}-k^3\tan^{-1}\left(\frac{b}{a}\sin\theta\right) \quad . \quad . \quad . \quad (447)$$

Let $$V=k^2\cos^2\theta+a^2+b^2\sin^2\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (448.)$$

and the last equation will become

$$3(A\Upsilon)=\int\frac{abk^2\cos^2\theta d\theta}{[a^2+b^2\sin^2\theta]\sqrt{V}}+\int\frac{2abkd\theta}{\sqrt{V}}+\frac{ab}{k}\int\frac{[a^2+b^2\sin^2\theta]}{\cos^2\theta\sqrt{V}}-k^3\tan^{-1}\left(\frac{b}{a}\sin\theta\right);$$

and this may be written in the form

$$\left.\begin{aligned}3(A\Upsilon)=\frac{ak^3(a^2+b^2)}{b}\int\frac{d\theta}{(a^2+b^2\sin^2\theta)\sqrt{V}}+\left[2abk-\frac{ak^3}{b}-\frac{ab^3}{k}\right]\int\frac{d\theta}{\sqrt{V}}\\ +\frac{ab}{k}(a^2+b^2)\int\frac{d\theta}{\cos^2\theta\sqrt{V}}-k^3\tan^{-1}\left(\frac{b}{a}\sin\theta\right)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (449.)$$

Let $$\frac{b^2}{a^2}=\tan^2\iota=n,\quad \frac{k^2-b^2}{k^2+a^2}=i^2,$$

and the preceding equation may be written

$$\left.\begin{aligned}3(A\Upsilon)=\frac{k^3(a^2+b^2)}{ab\sqrt{a^2+k^2}}\int\frac{d\theta}{[1+n\sin^2\theta]\sqrt{1-i^2\sin^2\theta}}\\ +\frac{ab(a^2+b^2)}{k\sqrt{a^2+k^2}}\int\frac{d\theta}{\cos^2\theta\sqrt{1-i^2\sin^2\theta}}-\frac{a}{bk}\frac{(k^2-b^2)^2}{\sqrt{a^2+k^2}}\int\frac{d\theta}{\sqrt{1-i^2\sin^2\theta}}-k^3\tan^{-1}\left(\frac{b}{a}\sin\theta\right)\end{aligned}\right\}. \quad (450.)$$

Since $$n=\frac{b^2}{a^2},\quad \frac{1+n}{n}=\frac{a^2+b^2}{b^2},$$

and as $(1-m)(1+n)=1-i^2$, $m=\frac{k^2}{a^2+k^2}$, and (47.) gives

$$\left(\frac{1+n}{n}\right)\int\frac{d\theta}{N\sqrt{\Gamma}}-\left(\frac{1-m}{m}\right)\int\frac{d\theta}{M\sqrt{\Gamma}}=\frac{i^2}{mn}\int\frac{d\theta}{\sqrt{\Gamma}}+\frac{1}{\sqrt{mn}}\tan^{-1}\left(\frac{\sqrt{mn}\sin\theta\cos\theta}{\sqrt{\Gamma}}\right),$$

hence

$$\left(\frac{1+n}{n}\right)\sqrt{mn}\int\frac{d\theta}{\mathrm{N}\sqrt{\mathrm{I}}}=\left(\frac{1-m}{m}\right)\sqrt{mn}\int\frac{d\theta}{\mathrm{M}\sqrt{\mathrm{I}}}+\frac{i^2}{\sqrt{mn}}\int\frac{d\theta}{\sqrt{\mathrm{I}}}+\tan^{-1}\left[\frac{\sqrt{mn}\sin\theta\cos\theta}{\sqrt{\mathrm{I}}}\right]. \quad (451.)$$

But

$$\left(\frac{1+n}{n}\right)\sqrt{mn}=\frac{k(a^2+b^2)}{ab\sqrt{a^2+k^2}}.$$

Hence

$$\left.\begin{aligned}\frac{3(\Delta\Upsilon)}{k^2}=&\frac{ab}{k\sqrt{k^2+a^2}}\int\frac{d\theta}{\left[1-\frac{k^2}{a^2+b^2}\sin^2\theta\right]\sqrt{\mathrm{I}}}\\&+\frac{ab(k^2-b^2)}{k^3\sqrt{k^2+a^2}}\int\frac{d\theta}{\sqrt{\mathrm{I}}}+\frac{ab(a^2+b^2)}{k^3\sqrt{k^2+a^2}}\int\frac{d\theta}{\cos^2\theta\sqrt{\mathrm{I}}}\\&+\tan^{-1}\left[\frac{\sqrt{mn}\sin\theta\cos\theta}{\sqrt{\mathrm{I}}}\right]-\tan^{-1}\left[\frac{b}{a}\sin\theta\right]\end{aligned}\right\} \quad (452.)$$

Now if Y be an arc of the plane hyperbola of which $\sqrt{k^2-b^2}$ is the transverse axis, and i the reciprocal of the eccentricity, we shall have

$$\frac{ab}{k^3}\mathrm{Y}=\frac{ab(a^2+b^2)}{k^3\sqrt{a^2+k^2}}\int\frac{d\theta}{\cos^2\theta\sqrt{\mathrm{I}}}. \quad (453.)$$

And if we take the spherical ellipse whose principal semiangles, α and β, are given by the equations

$$\cos\alpha=\frac{b}{k},\ \cos\beta=\frac{b}{k}\sqrt{\frac{k^2+a^2}{k^2+b^2}},$$

we shall have

$$\sin^2\varepsilon=\frac{k^2-b^2}{k^2+a^2},\ e^2=\frac{k^2}{k^2+a^2}$$

and

$$\frac{\tan\beta}{\tan\alpha}\cos\alpha=\frac{ab}{k\sqrt{k^2+a^2}};$$

also

$$\psi=\tan^{-1}\left(\frac{b}{a}\sin\theta\right).$$

Hence the sum of the first and last terms may be written

$$\left[\psi-\frac{\tan\beta}{\tan\alpha}\cos\alpha\int\frac{d\theta}{[1-e^2\sin^2\theta]\sqrt{1-\sin^2\varepsilon\sin^2\theta}}\right];$$

and this expression is S, the value of the area of the spherical ellipse ($\alpha\beta$), as shown at page 16 of the *Theory of Elliptic Integrals, &c.*

Now, as before, A being the transverse axe of the auxiliary hyperbola,

$$\mathrm{A}=\sqrt{k^2-b^2},\ \text{and}\ \mathrm{B}=\sqrt{a^2+b^2},$$

hence the coefficient of $\int\frac{d\theta}{\sqrt{\mathrm{I}}}$ may be written $\frac{ab}{k^3}\frac{\mathrm{A}^2}{\mathrm{B}}j$, and the equation (452.) finally assumes the form

$$3k(\Delta\Upsilon)=ab\left[\mathrm{Y}+\frac{\mathrm{A}^2}{\mathrm{B}}j\int\frac{d\theta}{\sqrt{\mathrm{I}}}\right]-k^3\mathrm{S}+k^3\tan^{-1}\left[\frac{\sqrt{mn}\sin\theta\cos\theta}{\sqrt{\mathrm{I}}}\right]. \quad (454.)$$

Or the area of the logarithmic hyperbola may be expressed as a sum of the arcs of

a common hyperbola, of a spherical ellipse, of a spherical parabola and of a circular arc, multiplied by constant coefficients.

LXXXVI. There is one particular case when the area of the logarithmic hyperbola may be represented by a very simple expression. Let $k=b$, then if we turn to (448.) $V=a^2+b^2$, and $I=1$, since $i=0$. Hence (452.) may be changed into

$$3(\Delta\Upsilon)=a\sqrt{a^2+b^2}\tan\theta+b^2\tan^{-1}\left(\frac{a}{\sqrt{a^2+b^2}}\tan\theta\right)$$

$$+b^2\tan^{-1}\left(\frac{b^2}{a\sqrt{a^2+b^2}}\sin\theta\cos\theta\right)-b^2\tan^{-1}\left(\frac{b}{a}\sin\theta\right);$$

and this expression may be reduced to

$$3(\Delta\Upsilon)=a\sqrt{a^2+b^2}\tan\theta+b^2\tan^{-1}\left(\frac{\sqrt{a^2+b^2}}{a}\tan\theta\right)-b^2\tan^{-1}\left(\frac{b}{a}\sin\theta\right), \quad . \quad . \quad . \quad . \quad (455.)$$

a value entirely independent of elliptic integrals, and which may be represented by a right line and the difference of two circular arcs.

LXXXVII. The curve of symmetrical intersection of a sphere by a paraboloid, whose principal sections are unequal, may be rectified by an elliptic integral of the third order and circular form.

Let $$x^2+y^2+z^2=2rz, \text{ and } \frac{x^2}{k}+\frac{y^2}{k_1}=2z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (456.)$$

be the equations of the sphere and paraboloid. Then finding the values of dx, dy and dz,

$$\left(\frac{ds}{dz}\right)^2=\frac{(r^2-kk_1)z-2r(r-k)(r-k_1)}{z[z-2(r-k)][2(r-k_1)-z]}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (457.)$$

Assume $$z=2(r-k)\cos^2\theta+2(r-k_1)\sin^2\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (458.)$$

Introducing the new variable θ and its functions,

$$\frac{ds}{d\theta}=2\frac{\sqrt{k_1(r-k)^2+k(r-k_1)^2\tan^2\theta}}{\sqrt{(r-k)+(r-k_1)\tan^2\theta}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (459.)$$

Assume $$k(r-k_1)^2\tan^2\theta=k_1(r-k)^2\tan^2\varphi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (460.)$$

then introducing the variable φ and its functions,

$$\frac{ds}{d\theta}=\frac{\sqrt{kk_1}\,\sqrt{(r-k)(r-k_1)}}{\sqrt{k(r-k_1)\cos^2\varphi+k_1(r-k)\sin^2\varphi}}$$

$$=\frac{\sqrt{k_1(r-k)}}{\sqrt{1-\frac{r}{k}\left(\frac{k-k_1}{r-k_1}\right)\sin^2\varphi}},$$

and $$\frac{d\theta}{d\varphi}=\frac{\sqrt{k_1(r-k)}}{\sqrt{k(r-k_1)}\left[1-\frac{(k-k_1)}{k}\frac{(r^2-kk_1)}{(r-k_1)^2}\sin^2\varphi\right]}. \quad . \quad . \quad . \quad . \quad . \quad (461.)$$

Hence integrating, $$s=\frac{k_1(r-k)^{\frac{3}{2}}}{\sqrt{k}(r-k_1)}\int\frac{d\varphi}{[1-m\sin^2\varphi]\sqrt{1-i^2\sin^2\varphi}}. \quad . \quad . \quad . \quad . \quad . \quad (462.)$$

If we write m for $\frac{k-k_1}{k}\left(\frac{r^2-kk_1}{(r-k_1)^2}\right)$, and i^2 for $\frac{k-k_1}{k}\frac{r}{r-k_1}$.

Now as $$i^2=\frac{\sin^2\alpha-\sin^2\beta}{\sin^2\alpha}, \text{ and } m=e^2=\frac{\sin^2\alpha-\sin^2\beta}{\sin^2\alpha\cos^2\beta}, \quad . \quad . \quad . \quad . \quad (463.)$$

we get from these equations

$$\tan^2\alpha=\frac{k(r-k_1)}{r(r-k)}, \ \tan^2\beta=\frac{k_1(r-k)}{r(r-k_1)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (464.)$$

whence $$\sqrt{r^2-kk_1}\,\frac{\tan\beta}{\tan\alpha}\sin\beta=\frac{k_1(r-k)^{\frac{3}{2}}}{\sqrt{k(r-k_1)}}.$$

Making these substitutions, (462.) will become

$$s=\sqrt{r^2-kk_1}\frac{\tan\beta}{\tan\alpha}\sin\beta\int_0^{\varphi}\frac{d\varphi}{[1-e^2\sin^2\varphi]\sqrt{1-\sin^2\alpha\sin^2\varphi}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (465.)$$

Now, as we have shown in (16.), this expression denotes an arc of the spherical ellipse whose principal angles are given by the equations (464.), and whose radius is $\sqrt{r^2-kk_1}$. Hence if a sphere be described whose radius is not r, but $\sqrt{r^2-kk_1}$, the length of the curve, the intersection of the sphere (r) with the paraboloid (kk_1) will be equivalent to that of a spherical ellipse described on the sphere whose radius is $\sqrt{r^2-kk_1}$.

When $r=k$, k being greater than k_1, (459.) becomes

$$\frac{ds}{d\theta}=2\sqrt{k(k-k_1)} \text{ or } s=2k(k-k_1)\theta.$$

Hence s is an arc of a circle. That such ought to be the case is manifest, for in this case the sphere intersects the paraboloid in its circular sections, and $\sqrt{\frac{k-k_1}{k}}$ is the cosine of the angle which the plane of the circular section of the paraboloid makes with its axis.

We have shown in the first part of this paper that the curves of intersection of *concentric* surfaces of the second order may be rectified by elliptic integrals. When the intersecting surfaces are not concentric, the rectification of the curve of intersection may be reduced to the integration of an expression which may be called an hyperelliptic integral.

The general expression for the length of an arc of this curve will be an integral of the form

$$s=\int dx\sqrt{\frac{\alpha x^4+\beta x^3+\gamma x^2+\delta x+\epsilon}{ax^4+bx^3+cx^2+ex+f}}.$$

When the surfaces are symmetrically placed and have a common plane of contact, the above expression may be reduced to

$$s=\int dx\sqrt{\frac{\alpha x^3+\beta x^2+\gamma x+\delta}{ax^3+bx^2+cx+e}}.$$

This is also an hyperelliptic integral.

When, moreover, the surfaces are concentric and symmetrically placed, the preceding expression may still further be simplified to

$$s=\int dx\sqrt{\frac{ax^3+\beta x+\gamma}{ax^2+bx+c}},$$

which is the general form for elliptic integrals.

We can perceive therefore that the solution of the general problem, to determine the length of the curve in which two surfaces of the second order may intersect, investigated under its most general form, far transcends the present powers of analysis. It is only when one of the surfaces becomes a plane, or when they are concentric and symmetrically placed, that the problem under these restricted conditions admits of a complete solution.

We may hence also surmise how vast are the discoveries which still remain to be explored in the wide regions of the integral calculus. We see how questions which arise from the investigation of problems based on the most elementary geometrical forms—surfaces of the second order—baffle the utmost powers of a refined analysis, with all the aids of modern improvement. It is not a little curious, that nearly all the branches of modern analysis, such as plane and spherical trigonometry, the doctrine of logarithms and exponentials, with the theory of elliptic integrals, may all be derived from the investigation of one geometrical problem,—To determine the length of an arc of the intersecting curve of two surfaces of the second order.

LXXXVIII. In the logarithmic hyperconic sections, we may develope properties analogous to those found in the spherical and plane sections, if we substitute parabolic arcs for arcs of great circles in the one, and for right lines in the other. Here follow a few of those theorems.

1. From any point on a parabolic section of the paraboloid let two parabolas be drawn touching the logarithmic ellipse or the logarithmic hyperbola, the parabolic arcs joining the points of contact will all pass through one point on the surface of the paraboloid.

2. If a hexagon, whose sides are parabolic arcs, be inscribed in a logarithmic ellipse or logarithmic hyperbola, the opposite parabolic arcs will meet two by two on a parabola.

3. If a hexagon, whose sides are parabolas, be circumscribed to a logarithmic ellipse, the parabolic arcs joining the opposite vertices will pass through a fixed point on the surface of the paraboloid.

4. If through the centre of a logarithmic ellipse or logarithmic hyperbola two parabolic arcs are drawn at right angles to each other, meeting the curve in two points, and parabolic arcs be drawn touching the curve in these points, they will meet on another logarithmic ellipse or logarithmic hyperbola.

5. If a circle, whose radius is a, be described on the surface of the paraboloid, and therefore touching the logarithmic ellipse or the logarithmic hyperbola at the extremities of its major axis, and from the extremities of any diameter two parabolic arcs

be drawn to any third point on the circle, if one of these parabolic arcs touches the logarithmic ellipse or the logarithmic hyperbola, the other will pass through a fixed point on the surface of the paraboloid.

6. If on the paraboloid we describe a circle whose radius is $\sqrt{a^2 \pm b^2}$, and if from the extremities of any diameter of this circle we draw parabolic arcs touching the logarithmic ellipse or the logarithmic hyperbola, these tangent parabolic arcs will meet on the circle.

These theorems will suffice. There would be little difficulty in extending the list. In fact nearly all the projective properties of right lines and conic sections on a plane may be transformed into analogous properties of great circles and spherical conic sections on the surface of a sphere, and of parabolic arcs and logarithmic sections on the surface of a paraboloid.

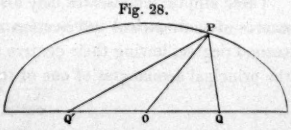
Section XII.—*On the Rectification of the Lemniscates.*

LXXXIX. There is a particular class of plane curves, of which the lemniscate of Bernoulli is an example, to which the principles established in the foregoing pages may be applied with much elegance.

Definition.—This entire class of curves may be defined by the following property. The square of the rectangle under the radii vectores drawn from the foci to any point on the curve is equal to a constant, plus or minus the square of the semidiameter multiplied by a constant quantity.

Let Q, Q′ be the foci, and O the centre, ϱ, ϱ_1, r the lines drawn from these points to any point on the curve. Let $OQ=OQ'=c$, and let f be a variable constant.

Fig. 28.



Then by the definition

$$\varrho^2\varrho_1^2=c^4\pm f^2r^2. \quad \ldots \quad (466.)$$

But $$\varrho^2\varrho_1^2=(x^2+y^2)^2+c^4+2c^2y^2-2c^2x^2,$$

and $$r^2=x^2+y^2,$$

hence $$(x^2+y^2)^2=(f^2+2c^2)x^2+(f^2-2c^2)y^2. \quad \ldots \quad (467.)$$

This is the general equation of the curve, which assumes different forms, as we assign varying values to f and c. Some examples may be given.

(a.) Let $c=0$, or $f=\infty$, the equation is that of a circle.

(b.) Let $f^2>2c^2$, and make $f^2+2c^2=a^2$, $f^2-2c^2=b^2$, $\quad \ldots \quad (468.)$

the equation will become $$(x^2+y^2)^2=a^2x^2+b^2y^2. \quad \ldots \quad (469.)$$

This is the equation of a curve which may be called the elliptic lemniscate. It is the locus, as is well known, of the intersection of central perpendiculars with tangents to an ellipse.

(c.) Let $f^2=2c^2$. The equation becomes $(x^2+y^2)^2=4c^2x^2$, or the equation is that of two equal circles in external contact.

(d.) Let $f^2<2c^2$. The equation becomes

$$(x^2+y^2)^2=(2c^2+f^2)x^2-(2c^2-f^2)y^2\text{; and } a^2>b^2.$$

(e.) Let $f^2=0$. The equation becomes $(x^2+y^2)^2=2c^2(x^2-y^2)$, or the equation is that of the lemniscate of Bernoulli.

(f.) Let f^2, passing through 0, be taken with a negative sign. The equation in this case becomes

$$(x^2+y^2)^2=(2c^2-f^2)x^2-(2c^2+f^2)y^2, \text{ and } b^2>a^2.$$

In one case only does the equation of the lemniscate in its general form coincide with that of Cassini's ellipse; namely, when $f=0$, and $h=c$, h^2 being the product of the radii vectores from the foci.

The definition of Cassini's ellipse being "a curve such that the product of the radii vectores drawn from two fixed points—the foci—to a third point on the curve, shall be constant and equal to h^2," its equation will obviously be, $2c$ being the distance between the foci,

$$h^4-c^4=(x^2+y^2)^2-2c^2(x^2-y^2),$$

when $$h=c, \quad (x^2+y^2)^2=2c^2(x^2-y^2).$$

This is the equation of the lemniscate of Bernoulli.

These elliptic lemniscates may also be defined as the orthogonal projections of the curves of symmetrical intersection of a paraboloid of revolution with cones of the second degree, having their centres at the vertex of the paraboloid. Let α and β be the principal semiangles of one of the cones. Its equation is

$$\cot^2\alpha.x^2 \pm \cot^2\beta.y^2=z^2.$$

Make $\tan\alpha=\frac{2k}{a}$, $\tan\beta=\frac{2k}{b}$, and the equation of the cone becomes

$$a^2x^2 \pm b^2y^2=4k^2z^2.$$

Let the equation of the paraboloid be $x^2+y^2=2kz$.

Eliminating z, the equation of the projection of the curve of intersection will become

$$(x^2+y^2)^2=a^2x^2 \pm b^2y^2.$$

XC. When the section is an ellipse, the equation of this curve is, as in (469.),

$$(x^2+y^2)^2=a^2x^2+b^2y^2. \quad \ldots\ldots\ldots\ldots \quad (470.)$$

This equation may be put in the form $r^2=a^2\cos^2\lambda+b^2\sin^2\lambda$,

r being the radius vector, and λ the angle it makes with the axis. Let s be an arc of this curve;

since $$\left(\frac{ds}{d\lambda}\right)^2=r^2+\left(\frac{dr}{d\lambda}\right)^2, \quad \left(\frac{ds}{d\lambda}\right)^2=\frac{a^4\cos^2\lambda+b^4\sin^2\lambda}{a^2\cos^2\lambda+b^2\sin^2\lambda}.$$

Assume $$\tan\lambda=\frac{a}{b}\tan\varphi. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (471.)$$

Making in the last equation the substitutions suggested by this transformation, we get, after some reductions,

$$b\frac{ds}{d\varphi}=\frac{a^2\cos^2\varphi+b^2\sin^2\varphi}{\left[1+\left(\frac{a^2-b^2}{b^2}\right)\sin^2\varphi\right]\sqrt{1-\left(\frac{a^2-b^2}{a^2}\right)\sin^2\varphi}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (472.)$$

Let $$\frac{a^2-b^2}{b^2}=n, \quad \frac{a^2-b^2}{a^2}=i^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (473.)$$

and the last equation will become

$$s=\frac{a^2+b^2}{b}\int\frac{d\varphi}{[1+n\sin^2\varphi]\sqrt{1-i^2\sin^2\varphi}}-b\int\frac{d\varphi}{\sqrt{1-i^2\sin^2\varphi}}. \quad . \quad . \quad . \quad . \quad (474.)$$

On the plane ellipse as a base, let a vertical cylinder be erected, and from the centre of this ellipse let a sphere with a radius $=\sqrt{a^2+b^2}$ be described. This sphere will cut the elliptic cylinder in a spherical conic section. The expression for an arc of a spherical conic section measured from the extremity of the *minor arc* is given by the equation

$$\frac{\bar{s}}{R}=\frac{\cos\beta}{\cos\alpha\sin\alpha}\int\frac{d\varphi}{[1+\tan^2\varepsilon\sin^2\varphi]\sqrt{1-\sin^2\eta\sin^2\varphi}}-\frac{\cos\alpha\cos\beta}{\sin\alpha}\int\frac{d\varphi}{\sqrt{1-\sin^2\eta\sin^2\varphi}}.$$

See Theory of Elliptic Integrals, p. 27.

Now in this case α and β being the principal angles of the concentric cone whose base is the spherical conic section,

$$\sin^2\alpha=\frac{a^2}{a^2+b^2}, \quad \sin^2\beta=\frac{b^2}{a^2+b^2},$$

therefore $$\cos^2\alpha=\frac{b^2}{a^2+b^2}, \quad \cos^2\beta=\frac{a^2}{a^2+b^2}.$$

Hence $$\alpha+\beta=\frac{\pi}{2},$$

or the sum of the principal angles of this cone is equal to two right angles, or the cone is its own supplemental cone. From these equations we may infer that

$$\frac{\cos\beta}{\cos\alpha\sin\alpha}=\frac{\sqrt{a^2+b^2}}{b}, \quad \frac{\cos\alpha\cos\beta}{\sin\alpha}=\frac{b}{\sqrt{a^2+b^2}}$$

$$\tan^2\varepsilon=\frac{\sin^2\alpha-\sin^2\beta}{\cos^2\alpha}=\frac{a^2-b^2}{b^2}, \quad \sin^2\eta=\frac{\sin\alpha-\sin^2\beta}{\sin\alpha}=\frac{a^2-b^2}{a^2}.$$

Making these substitutions in the preceding equation, we get

$$\bar{s}=\frac{a^2+b^2}{b}\int\frac{d\varphi}{\left[1+\left(\frac{a^2-b^2}{b^2}\right)\sin^2\varphi\right]\sqrt{1-\left(\frac{a^2-b^2}{a^2}\right)\sin^2\varphi}}-b\int\frac{d\varphi}{\sqrt{1-\left(\frac{a^2-b^2}{a^2}\right)\sin^2\varphi}}.$$

On comparing this equation with (474.) we shall see that they are precisely identical. Whence we infer that an arc of the elliptic lemniscate is equal to an arc of a spherical ellipse which is self-supplemental. It is very remarkable, that, whatever be the ratio of a to b the semiaxes of the plane ellipse or of the elliptic lemniscate, the arc is always equal to an arc of this particular species of spherical ellipse.

There is another property of this spherical ellipse, that its area, together with twice the lateral surface of the cone, is equal to a hemisphere. See Theory of Elliptic Integrals, &c., p. 21.

XCI. We may obtain under another form an expression for the arc of an elliptic lemniscate.

Let the polar angle λ be measured from the minor axis of the curve. Its equation in this case will be

$$r^3=a^3\sin^3\lambda+b^3\cos^3\lambda,$$

$$\therefore\ \frac{ds^2}{d\lambda^2}=\frac{a^4\sin^2\lambda+b^4\cos^2\lambda}{a^3\sin^3\lambda+b^3\cos^3\lambda}.$$

Assume $$\tan\lambda=\frac{b^2}{a^2}\tan\psi, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (475.)$$

hence $$\frac{ds^2}{d\lambda^2}=\frac{a^2b^2}{a^3\cos^2\psi+b^3\sin^2\psi}, \text{ and } \frac{d\lambda}{d\psi}=\frac{a^2b^2}{a^4\cos^2\psi+b^4\sin^2\psi},$$

integrating, $$s=\frac{b^3}{a^2}\int\frac{d\psi}{\left[1-\left(\frac{a^4-b^4}{a^4}\right)\sin^2\psi\right]\sqrt{1-\left(\frac{a^2-b^2}{a^2}\right)\sin^2\psi}}. \quad \ldots\ldots \quad (476.)$$

Let, as before, a cylinder be erected on the ellipse and the sphere described from its centre with a radius equal to $\sqrt{a^2+b^2}$, it will cut the cylinder in a spherical ellipse, whose arc is given by the integral

$$\frac{\bar{s}}{k}=\frac{\tan\beta}{\tan\alpha}\sin\beta\int\frac{d\psi}{\left[1-\left(\frac{\tan^2\alpha-\tan^2\beta}{\tan^2\alpha}\right)\sin^2\psi\right]\sqrt{1-\left(\frac{\sin^2\alpha-\sin^2\beta}{\sin^2\alpha}\right)\sin^2\psi}}.$$

Now since $$\sin^2\alpha=\frac{a^2}{a^2+b^2},\ \sin^2\beta=\frac{b^2}{a^2+b^2}$$

$$k\frac{\tan\beta}{\tan\alpha}\sin\beta=\frac{b^3}{a^2},\ \frac{\tan^2\alpha-\tan^2\beta}{\tan^2\alpha}=\frac{a^4-b^4}{a^4},\ \frac{\sin^2\alpha-\sin^2\beta}{\sin^2\alpha}=\frac{a^2-b^2}{a^2},$$

substituting, we obtain $$\bar{s}=\frac{b^3}{a^2}\int\frac{d\psi}{\left[1-\left(\frac{a^4-b^4}{a^4}\right)\sin^2\psi\right]\sqrt{1-\left(\frac{a^2-b^2}{a^2}\right)\sin^2\psi}}.$$

Now this is precisely the same equation as (476.), whence we infer that the arc of the elliptic lemniscate is equal to an arc of a self-supplemental spherical ellipse. Writing m for the parameter in this expression, we can easily show that the parameters in this and the preceding formula (474.) are *conjugate* parameters. The con-

dition of the conjugation of parameters in the circular form is

$$(1+n)(1-m)=(1-i^2).$$

Now $$1+n=\frac{a^2}{b^2},\ 1-m=\frac{b^4}{a^4},\ 1-i^2=\frac{b^2}{a^2},$$

whence the proposition is manifest.

An invariable relation exists between the parameter m and the modulus i; for as

$$m=\frac{a^4-b^4}{a^4} \text{ and } i^2=\frac{a^2-b^2}{a^2} \quad \frac{m}{i^2}+i^2=2, \quad \ldots\ldots\ldots \quad (477.)$$

hence i being given, m also is given; or the elliptic lemniscate can be represented by only one species of spherical ellipse, that in which the sum of the principal arcs is equal to two right angles.

On the Hyperbolic Lemniscate.

XCII. The equation of the lemniscate in this case is

$$(x^2+y^2)^2=a^2x^2-b^2y^2.$$

Following the steps indicated in (XC.), we find

$$\frac{ds^2}{d\lambda^2}=\frac{a^4\cos^2\lambda+b^4\sin^2\lambda}{a^2\cos^2\lambda-b^2\sin^2\lambda};$$

the limits of λ are 0 and $\tan^{-1}\frac{a}{b}$.

Assume $$\sin^2\lambda=\frac{a^4\sin^2\varphi}{a^2b^2+a^4\sin^2\varphi+b^4\cos^2\varphi}. \quad \ldots\ldots\ldots \quad (478.)$$

The limits of φ, corresponding to $\lambda=0$ and $\lambda=\tan^{-1}\frac{a}{b}$, are $\varphi=0$, and $\varphi=\frac{\pi}{2}$.

Substituting this value of $\sin^2\lambda$ in the preceding equation, we shall find

$$\frac{ds}{d\lambda}=\frac{a}{\cos\varphi}. \quad \ldots\ldots\ldots\ldots\ldots \quad (479.)$$

From (478.) we may derive

$$\frac{d\lambda}{d\varphi}=\frac{a^2b(a^2+b^2)\cos\varphi}{[a^2b^2+a^4\sin^2\varphi+b^4\cos^2\varphi]\sqrt{a^2+b^2\cos^2\varphi}}.$$

Multiplying the two latter equations together and reducing, we get

$$s=\frac{a^2}{b\sqrt{a^2+b^2}}\int\frac{d\varphi}{\left[1+\left(\frac{a^2-b^2}{b^2}\right)\sin^2\varphi\right]\sqrt{1-\frac{b^2}{a^2+b^2}\sin^2\varphi}}. \quad \ldots\ldots \quad (480.)$$

When $a=b$, or when the lemniscate is that of Bernoulli, we get the well-known expression

$$s=\frac{a}{\sqrt{2}}\int\frac{d\varphi}{\sqrt{1-\frac{1}{2}\sin^2\varphi}}.$$

When $a>b$ the integral is of the third order and *circular* form, but when $a<b$ the integral is of the third order and *logarithmic* form. That it is of the logarithmic form may thus be shown.

Let $$\frac{b^2-a^2}{b^2}=m, \text{ and } i^2=\frac{b^2}{a^2+b^2}.$$

Hence $$i^2-m=\frac{a^4}{b^2(a^2+b^2)};$$

or i^2 is greater than m; but we know that the form is logarithmic when the square of the modulus is greater than the parameter, when it is affected with a negative sign.

This is a result truly remarkable. All analysts know the impossibility of transforming the circular form into the logarithmic, or *vice versâ*, by any other than an imaginary transformation. The utmost efforts of the most accomplished analysts have been exhausted in the attempt; yet in this particular case their geometrical connection is very close. The modulus and the parameter are connected by the equation

$$\frac{1}{i^2}+m=2; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (481.)$$

the upper sign to be taken in the circular form, the lower in the logarithmic.

There are two distinct cases to be considered; when a is greater than b, and when a is less than b.

Case I. $a>b$.

Let a plane ellipse be constructed whose principal semiaxes A and B are given by the equations

$$A^2=a^2+b^2, \quad B^2=a^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (482.)$$

and let a sphere be described from the centre of this ellipse with a radius

$$=\frac{a^2}{\sqrt{a^2-b^2}}=\frac{B^2}{\sqrt{2B^2-A^2}}=R.$$

Then we can find, as follows, the length of an arc of the spherical ellipse, the intersection of the sphere whose radius is R, with the cylinder standing on the ellipse whose semiaxes are A and B.

Since $$\sin^2\alpha=\frac{A^2}{R^2}=\frac{a^4-b^4}{a^4}, \quad \cos^2\alpha=\frac{b^4}{a^4},$$

and $$\sin^2\beta=\frac{B^2}{R^2}=\frac{a^2-b^2}{a^2}, \quad \cos^2\beta=\frac{b^2}{a^2},$$

$$\therefore \frac{R\cos\beta}{\cos\alpha\sin\alpha}=\frac{a^5}{b(a^2-b^2)\sqrt{a^2+b^2}}.$$

We have also

$$\left.\begin{aligned} &\frac{R\cos\beta\cos\alpha}{\sin\alpha}=\frac{ab^2}{(a^2-b^2)\sqrt{a^2+b^2}} \\ &\tan^2\varepsilon=\frac{\cos^2\beta-\cos^2\alpha}{\cos^2\alpha}=\frac{a^2-b^2}{b^2} \\ &i^2=\sin^2\eta=\frac{\sin^2\alpha-\sin^2\beta}{\sin^2\alpha}=\frac{b^2}{a^2+b^2} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (483.)$$

Substituting these values in (46.) the expression for an arc of a spherical ellipse with a *positive* parameter, and writing $\bar{s}$ for the arc, we get

$$\left.\begin{aligned}\frac{a^2-b^2}{a^2}\bar{s}=&\frac{a^3}{b\sqrt{a^2+b^2}}\int\frac{d\varphi}{\left[1+\left(\frac{a^2-b^2}{b^2}\right)\sin^2\varphi\right]\sqrt{1-\frac{b^2}{a^2+b^2}\sin^2\varphi}}\\&-\frac{b^3}{a\sqrt{a^2+b^2}}\int\frac{d\varphi}{\sqrt{1-\frac{b^2}{a^2+b^2}\sin^2\varphi}}-\sqrt{a^2-b^2}\tau.\end{aligned}\right\}\quad\ldots\quad(484.)$$

Comparing this with (480.), we find

$$s-\left(\frac{a^2-b^2}{a^2}\right)\bar{s}=\frac{b^3}{a\sqrt{a^2+b^2}}\int\frac{d\varphi}{\sqrt{1-\left(\frac{b^2}{a^2+b^2}\right)\sin^2\varphi}}+\sqrt{a^2-b^2}\tau,$$

or the *difference* between an arc of a hyperbolic lemniscate and an arc of a spherical ellipse may be expressed by an integral of the first order, together with a circular arc. When $a=b$, the radius of the sphere is infinite, the sphere becomes a plane, so that it is not possible to express an arc of a spherical ellipse by the common lemniscate.

Case II. Let $b>a$.

In this case the arc of the hyperbolic lemniscate may be expressed by an arc of a logarithmic ellipse of a *particular species*, or one whose parameter and modulus are connected by the relation given in (481.).

Resuming the expression in (480.) for the arc of the hyperbolic lemniscate,

$$s=\frac{a^3}{b\sqrt{a^2+b^2}}\int\frac{d\varphi}{\left[1-\left(\frac{b^2-a^2}{b^2}\right)\sin^2\varphi\right]\sqrt{1-\frac{b^2}{b^2+a^2}\sin^2\varphi}}.$$

Let
$$\left.\begin{aligned}&\frac{b^2-a^2}{b^2}=m,\quad\frac{b^2}{b^2+a^2}=i^2,\\&\text{then as}\qquad m+n-mn=i^2,\quad n=\frac{a^2}{a^2+b^2}\end{aligned}\right\}\quad\ldots\quad(485.)$$

Let A and B be the semiaxes of the base of the elliptic cylinder, k the parameter of the paraboloid whose intersection with the cylinder gives the logarithmic ellipse. Assume for the principal semimajor axis of the elliptic base

$$\mathrm{A}=\sqrt{a^2+b^2}.\quad\ldots\quad(486.)$$

In (171.) we found the following relations between A, B, k, m, n,

$$\frac{\mathrm{A}^2}{k^2}=\frac{mn(1-n)}{(n-m)^2},\quad\frac{\mathrm{B}^2}{k^2}=\frac{mn(1-m)}{(n-m)^2},$$

and as we assume $\mathrm{A}=\sqrt{a^2+b^2}$, we get, substituting for m and n their values in terms of a and b, the semiaxes of the hyperbola

$$\mathrm{B}=\frac{b^2}{a},\text{ and }k=\frac{a^2b^2+a^4-b^4}{a^2\sqrt{b^2-a^2}}.\quad\ldots\quad(487.)$$

In (163.) we found for the equation of the logarithmic ellipse measured from the *minor* axis, and multiplied by the indeterminate factor Q,

$$\left.\begin{aligned} 2\mathrm{Q}\Sigma = &-\left(\frac{1-m}{m}\right)\sqrt{mn}k\mathrm{Q}\int\frac{d\varphi}{[1-m\sin^2\varphi]\cdot\sqrt{1-i^2\sin^2\varphi}} \\ &+\frac{k\mathrm{Q}\sqrt{mn}}{n-m}\left[\int d\varphi\sqrt{\Delta}+\left(\frac{i^2-m}{m}\right)\int\frac{d\varphi}{\sqrt{\Delta}}-m\Phi\right] \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (488.)$$

If in this equation we substitute for m, n, and k their values as given in (485.), and equate the coefficient $\left(\frac{1-m}{m}\right)\sqrt{mn}k\mathrm{Q}$ with the coefficient $\frac{a^2}{b\sqrt{a^2+b^2}}$ of the expression for the lemniscate in (480.), we shall find

$$\mathrm{Q}=\frac{a^2(b^2-a^2)}{a^2b^2+a^4-b^4};$$

hence the last equation, substituting this value of Q, will become

$$\begin{aligned} \frac{2a^2(b^2-a^2)}{a^2b^2+a^4-b^4}\Sigma+s=&\frac{ab(b^2-a^2)\sqrt{a^2+b^2}}{a^2b^2+a^4-b^4}\int d\varphi\sqrt{\Delta} \\ &+\frac{a^2b}{[a^2b^2+a^4-b^4]\sqrt{a^2+b^2}}\int\frac{d\varphi}{\sqrt{\Delta}}-\frac{a(b^2-a^2)^2\sqrt{a^2+b^2}}{b(a^2b^2+a^4-b^4)}\Phi; \quad . \quad . \quad . \quad (489.) \end{aligned}$$

or the *sum* of an arc of a hyperbolic lemniscate and of an arc of a logarithmic ellipse may be expressed as a sum of integrals of the first and second orders with a circular arc.

When $b=a$, the above expression will become

$$s=\frac{a}{\sqrt{2}}\int\frac{d\varphi}{\sqrt{1-\frac{1}{2}\sin^2\varphi}}.$$

In this case the parameter of the paraboloid becomes infinite, and therefore the paraboloid a plane, just as the sphere became a plane in the last case; so that we cannot express integrals of the third order, whether circular or logarithmic, by an arc of a common lemniscate.

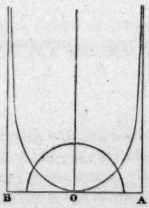
XCIII. FAGNANI, the Italian geometer, first showed that the lemniscate of the equilateral hyperbola might be rectified by an elliptic integral of the first order whose modulus is $\frac{1}{\sqrt{2}}$. He did not however extend his researches to the investigation of the general problem of the rectification of the lemniscates.

Although the lemniscates may be rectified by elliptic integrals of the third order, as well circular as logarithmic, yet these curves cannot be accepted as general representatives of integrals of the third order, because in the functions which represent those curves, the parameters and the moduli are connected by an invariable relation, as in (477.) and (481.). Thus the elliptic lemniscate, whatever be the ratio of the axes of the generating plane ellipse, can be represented only by a particular species of spherical ellipse, that whose principal arcs are supplemental.

XCIV. The general fundamental expressions for the rectification of curve lines, whether of single or double flexion, show that the arc of a curve may in general be represented as the sum of two quantities, an integrated and a non-integrated part, or as the proposition may be more briefly put, an arc of a curve may be expressed as the sum of an integral and a residual. Thus the arc of a plane ellipse is equal to an integral and a residual, which latter is a right line. An arc of a parabola is the sum of an integral and a residual, which latter is also a right line. An arc of a spherical ellipse is the sum of an integral and a residual, the latter being an arc of a circle, while an arc of a logarithmic ellipse is made up of two portions, one a sum of integrals, the other—the residual—being an arc of a common parabola. It appears therefore to be an expenditure of skill in a wrong direction to devise curves whose arcs should differ from the corresponding arcs of hyperconic sections by the above-named residuals. Thus geometers have sought to discover plane curves whose arcs should be represented by elliptic integrals of the first order, without any residual quantity—the common lemniscate for example, when the modulus has a particular value. It is possible that such may be found. In the same way, an exponential* curve may be devised, whose arc shall be represented by the integral $k\int\frac{d\theta}{\cos\theta}$, instead of taking it with the residual quantity $k\tan\theta\sec\theta$, as the expression for an arc of a common parabola. Thus geometers have been led to look for the types of elliptic integrals among the higher orders of plane curves, overlooking the analogy which points to the intersection of surfaces of the second order as the natural geometrical types of those integrals.

* The equation of this exponential curve is $e^{\frac{y}{k}}\cos\left(\frac{x}{k}\right)=1$. It is easily seen that when $x=0$, $y=0$, also. And when $x=\frac{k\pi}{2}$, $y=\infty$. Hence the curve passes through the origin and has asymptots parallel to the axis of y at the distance $\frac{k\pi}{2}$ from the origin.

Fig. 29.



If we substitute for $\cos\left(\frac{x}{k}\right)$ its exponential expression $\frac{e^{\frac{x}{k}\sqrt{-1}}+e^{-\frac{x}{k}\sqrt{-1}}}{2}$, the equation of the curve becomes $\left[e^{\frac{y+x\sqrt{-1}}{k}}-1\right]+\left[e^{\frac{y-x\sqrt{-1}}{k}}-1\right]=0$.

The common equation of the circle $y^2+x^2=k^2$, may be written

$$\log\left[\frac{y+x\sqrt{-1}}{k}\right]+\log\left[\frac{y-x\sqrt{-1}}{k}\right]=0.$$

In this form the similarity of the equations of the exponential curve and the circle is evident.

In the equation $s=k\int\frac{d\theta}{\cos\theta}$, if we make the imaginary transformation $\tan\theta=\sqrt{-1}\sin\omega$, the resulting expression will be $s=k\omega\sqrt{-1}$, or the expression is transformed from a logarithmic to a circular function.

V. *On a Class of Differential Equations, including those which occur in Dynamical Problems.—Part I.* *By* W. F. Donkin, *M.A., F.R.S., F.R.A.S., Savilian Professor of Astronomy in the University of Oxford.*

Received February 23,—Read February 23, 1854.

THE Analytical Theory of Dynamics, as it exists at present, is due mainly to the labours of Lagrange, Poisson, Sir W. R. Hamilton, and Jacobi; whose researches on this subject present a series of discoveries hardly paralleled, for their elegance and importance, in any other branch of mathematics.

The following investigations in the same department do not pretend to make any important step in advance; though I should not of course have presumed to lay them before the Society, if I had not hoped they might be found to possess some degree of novelty and interest*.

Of previous publications with which I am acquainted, those most nearly on the same subject are, Sir W. R. Hamilton's two memoirs "On a General Method in Dynamics" in the Philosophical Transactions; Jacobi's Memoir in the 17th vol. of Crelle's Journal, "Ueber die Reduction der partiellen Differential-gleichungen," &c.; and M. Bertrand's "Mémoire sur l'integration des équations différentielles de la Mécanique," in Liouville's Journal (1852). The relation in which the present essay stands to the papers just named will be apparent to those who are acquainted with them, and it would be useless to attempt to make it intelligible to others.

Oxford, Feb. 21, 1854.

Section I.

1. Let $x_1, x_2, \ldots x_n$ be n variables, connected by n relations with n other variables $y_1, y_2, \ldots y_n$; so that each variable of either set may be considered as a function of the variables of the other set. Suppose then

$$y_i = \varphi_i(x_1, x_2, \ldots x_n),$$

[* It may be useful to specify the parts to which I should principally refer as containing what is, relatively to my own reading on the subject, new; and in the present day it can hardly be required of any one to profess more than this kind of originality. These are—the theorem (3.), art. 1. The results of arts. 2 to 4. The formulæ (19.), art. 7. The general form of the theorem (26.), art. 10. The processes and results of arts. 12 to 14. The generalization of Sir W. Hamilton's transformation of the dynamical equations, arts. 17, 18. The demonstration of Poisson's theorem, arts. 21, 22. The contents of art. 25. The method of obtaining elliptic elements, arts. 27 to 30. The contents of arts. 34 to 36. The solution of the problem of rotation, Section III.]

this equation would become identical if $x_1, x_2, \ldots x_n$, in its second member, were expressed in terms of $y_1, y_2, \ldots y_n$; hence, differentiating each side, on this hypothesis, first with respect to y_i, and then with respect to y_j, we obtain

$$1=\frac{dy_i}{dx_1}\frac{dx_1}{dy_i}+\frac{dy_i}{dx_2}\frac{dx_2}{dy_i}+\ldots+\frac{dy_i}{dx_n}\frac{dx_n}{dy_i} \quad \ldots\ldots\ldots\ldots \quad (1.)$$

$$0=\frac{dy_i}{dx_1}\frac{dx_1}{dy_j}+\frac{dy_i}{dx_2}\frac{dx_2}{dy_j}+\ldots+\frac{dy_i}{dx_n}\frac{dx_n}{dy_j}, \quad \ldots\ldots\ldots\ldots \quad (2.)$$

where j is any index different from i. These theorems are given by JACOBI in his memoir "De Determinantibus functionalibus." They are however only particular cases of more general theorems, which may be investigated as follows.

If we represent by

$$i, j, k, \ldots.$$

$$p, q, r, \ldots.$$

any two determinate sets of m indices each, selected out of the series $1, 2, 3, \ldots n$, then the determinant formed with the m^2 differential coefficients

$$\frac{dy_i}{dx_p}, \frac{dy_i}{dx_q}, \ldots.; \frac{dy_j}{dx_p}, \frac{dy_j}{dx_q}, \ldots; \&c.$$

possesses properties remarkably analogous to those of a simple differential coefficient. This analogy was pointed out by JACOBI, and has been further developed by M. BERTRAND in his "Mémoire sur le Déterminant d'un système de Fonctions" (LIOUVILLE'S Journal, 1851).

It appears to me that such functional determinants might be appropriately and conveniently denoted by a symbol analogous to that of a common differential coefficient; thus

$$\frac{d(y_i, y_j, y_k, \ldots)}{d(x_p, x_q, x_r, \ldots)}, \quad \ldots\ldots\ldots\ldots \quad (D.)$$

and I shall adopt this notation in the present paper. For example,

$$\frac{d(u, v)}{d(x, y)}$$

would represent the determinant

$$\frac{du}{dx}\frac{dv}{dy}-\frac{du}{dy}\frac{dv}{dx}.$$

[The expression (D.) is not a mere arbitrary symbol, but, like a simple differential coefficient, is a *real fraction*. For if we denote by

$$d(x_p, x_q, x_r, \ldots)$$

the determinant formed with the m^2 quantities

$$d_1x_p, d_1x_q, d_1x_r, \ldots.$$

$$d_2x_p, d_2x_q, d_2x_r, \ldots$$

$$\ldots\ldots\ldots$$

$$d_mx_p, d_mx_q d_m, x_r, \ldots.$$

and attribute a corresponding meaning to

$$d(y_i, y_j, y_k, \ldots),$$

where $d_1, d_2, \ldots d_n$ are symbols denoting n distinct and independent sets of variations, so that

$$d_s y_i = \frac{dy_i}{dx_1} d_s x_1 + \frac{dy_i}{dx_2} d_s x_2 + \ldots + \frac{dy_i}{dx_n} d_s x_n,$$

then it follows from well-known properties of determinants (as M. BERTRAND has shown) that the complete functional determinant formed with the n^2 differential coefficients

$$\frac{dy_1}{dx_1}, \frac{dy_1}{dx_2}, \ldots, \frac{dy_2}{dx_1}, \frac{dy_2}{dx_2}, \ldots \text{ \&c.}$$

is equal to the quotient of the two determinants which I propose to denote by

$$d(y_1, y_2, y_3, \ldots y_n), \quad d(x_1, x_2, x_3, \ldots x_n),$$

and moreover that the partial functional determinant formed with the m^2 terms

$$\frac{dy_i}{dx_p}, \frac{dy_i}{dx_q}, \ldots, \frac{dy_j}{dx_p}, \frac{dy_j}{dx_q}, \ldots, \text{ \&c.}$$

is equal to the quotient of the two partial determinants

$$d(y_i, y_j, y_k, \ldots), d(x_p, x_q, x_r, \ldots),$$

the differentials of y_i, &c. being taken on the hypothesis that all the differentials of the x-variables are $=0$, except those of the set $x_p, x_q, x_r, \ldots$. Thus the expression (D.) is a real fraction, provided its numerator and denominator be interpreted in a manner exactly analogous to that in which the numerator and denominator of an ordinary total or partial differential coefficient are interpreted.]

This being premised, let $u_1, u_2, \ldots u_m$ be m functions of any or all of the functions $y_1, y_2, \ldots y_n$ (m being supposed not greater than n), so that u_1, u_2, &c. are functions of x_1, x_2, &c. through y_1, y_2, &c.

Let any selected sets of m indices out of the series $1, 2, \ldots n$, be denoted, for greater clearness, by $\alpha_1, \alpha_2, \ldots \alpha_m$; $\beta_1, \beta_2, \ldots \beta_m$, &c. Then the general theorem analogous to

$$du_i = \frac{du_i}{dy_1} dy_1 + \frac{du_i}{dy_2} dy_2 + \text{\&c.}$$

may be expressed as follows:—

$$d(u_{\alpha_1}, u_{\alpha_2}, \ldots, u_{\alpha_m}) = \Sigma_\beta \left\{ \frac{d(u_{\alpha_1}, u_{\alpha_2}, \ldots, u_{\alpha_m})}{d(y_{\beta_1}, y_{\beta_2}, \ldots, y_{\beta_m})} d(y_{\beta_1}, y_{\beta_2}, \ldots, y_{\beta_m}) \right\}$$

(the summation on the second side referring only to the indices β, and extending to every combination of m out of the n numbers $1, 2, \ldots n$).

In like manner, the theorem analogous to

$$\frac{du_i}{dx_j} = \frac{du_i}{dy_1} \frac{dy_1}{dx_j} + \frac{du_i}{dy_2} \frac{dy_2}{dx_j} + \ldots$$

is

$$\frac{d(u_{\alpha_1}, u_{\alpha_2}, \ldots u_{\alpha_m})}{d(x_{\gamma_1}, x_{\gamma_2}, \ldots x_{\gamma_m})} = \Sigma_\beta \left\{ \frac{d(u_{\alpha_1}, u_{\alpha_2}, \ldots u_{\alpha_m})}{d(y_{\beta_1}, y_{\beta_2}, \ldots y_{\beta_m})} \cdot \frac{d(y_{\beta_1}, y_{\beta_2}, \ldots y_{\beta_m})}{d(x_{\gamma_1}, x_{\gamma_2}, \ldots x_{\gamma_m})} \right\}.$$

These two theorems (expressed in a different notation) may be found in the memoirs above cited. But the following, which we shall have occasion to employ hereafter, has not, so far as I am aware, been explicitly stated.

Inasmuch as $\frac{dy_i}{dy_i}=1$, $\frac{dy_i}{dy_j}=0$, it follows that the determinant represented by

$$\frac{d(y_{\alpha_1}, y_{\alpha_2}, \dots y_{\alpha_m})}{d(y_{\beta_1}, y_{\beta_2}, \dots y_{\beta_m})} \quad \dots\dots\dots\dots \quad (E.)$$

is $=1$ if $\beta_1, \beta_2, \dots \beta_m$ be the *same combination of indices* as $\alpha_1, \alpha_2, \dots \alpha_m$, but is $=0$ in every other case. (For in the first case the determinant is formed with 1, 0, 0, ...; 0, 1, 0, ...; 0, 0, 1, ...; &c., but if there be one index β_i which is not contained in the series α_1, α_2, &c., then one row of terms in the determinant will consist wholly of zeros.)

Now considering y_1, y_2, &c. as functions of x_1, x_2, &c., and again considering these latter as functions of y_1, y_2, &c. given by the inverse equations, we have, by the preceding theorem, for the value of the determinant (E.) above written, the expression $\nabla_m=$

$$\Sigma_\gamma \left\{ \frac{d(y_{\alpha_1}, y_{\alpha_2}, \dots y_{\alpha_m})}{d(x_{\gamma_1}, x_{\gamma_2}, \dots x_{\gamma_m})} \cdot \frac{d(x_{\gamma_1}, x_{\gamma_2}, \dots x_{\gamma_m})}{d(y_{\beta_1}, y_{\beta_2}, \dots y_{\beta_m})} \right\}$$

(where $\alpha_1, \alpha_2, \dots \alpha_m$; $\beta_1, \beta_2, \dots \beta_m$ are two *determinate* sets of m out of the n indices, and the summation with respect to the indices γ extends to every combination of m out of the n). Consequently,

$$\nabla_m=1 \text{ or } \nabla_m=0, \quad \dots\dots\dots\dots \quad (3.)$$

according as the series of indices

$$\beta_1, \beta_2, \dots \beta_m$$

is, or is not, the same combination as

$$\alpha_1, \alpha_2, \dots \alpha_m.$$

(I suppose, for convenience, that when the two *combinations* are the same, *the arrangement* is the same in each; otherwise the value of ∇_m may be -1.)

This is the theorem in question. If we put $m=1$, we obtain the equations (1.) and (2.) given at the beginning of this article. If we put $m=n$, the expression ∇_n reduces itself to the product of the two determinants formed respectively with the *complete* sets of differential coefficients $\frac{dy_i}{dx_j}$ &c., $\frac{dx_i}{dy_j}$ &c., the value of which product is $=1$, as is well known.

As an illustration, it may be useful to exhibit the theorem in the case of $m=2$, as expressed by the common notation. Namely,

$$\nabla_2=\Sigma \left\{ \left(\frac{dy_p}{dx} \frac{dy_q}{dx_j} - \frac{dy_p}{dx_j} \frac{dy_q}{dx_i} \right) \left(\frac{dx_i}{dy_\alpha} \frac{dx_j}{dy_\beta} - \frac{dx_i}{dy_\beta} \frac{dx_j}{dy_\alpha} \right) \right\}=1, \text{ or } =0, \quad \dots \quad (4.)$$

according as α, β are, or are not, the same as p, q. Here α, β; p, q are two determinate pairs of indices, and the summation refers to i, j, extending to every binary combination.

2. *Theorem.*—Retaining the suppositions made at the beginning of the last article, let X be a given function of $x_1, x_2, \ldots x_n$; and let us further suppose that the equations by which $y_1, y_2, \ldots y_n$ are determined as functions of x_1, &c., are

$$y_1=\frac{dX}{dx_1},\ y_2=\frac{dX}{dx_2},\ \ldots\ldots,\ y_n=\frac{dX}{dx_n}, \quad \ldots\ldots\ldots \quad (5.)$$

so that $$\frac{dy_i}{dx_j}=\frac{dy_j}{dx_i};$$

and if we transform the equations (1.), (2.), art. 1, by this condition, we obtain the n equations

$$\frac{dy_1}{dx_1}\frac{dx_1}{dy_i}+\frac{dy_2}{dx_1}\frac{dx_2}{dy_i}+\ldots+\frac{dy_n}{dx_1}\frac{dx_n}{dy_i}=0$$

$$\frac{dy_1}{dx_2}\frac{dx_1}{dy_i}+\frac{dy_2}{dx_2}\frac{dx_2}{dy_i}+\ldots+\frac{dy_n}{dx_2}\frac{dx_n}{dy_i}=0$$

$$\ldots\ldots\ldots\ldots$$

$$\frac{dy_1}{dx_i}\frac{dx_1}{dy_i}+\frac{dy_2}{dx_i}\frac{dx_2}{dy_i}+\ldots+\frac{dy_n}{dx_i}\frac{dx_n}{dy_i}=1$$

$$\ldots\ldots\ldots\ldots$$

If these equations be added, after multiplying them respectively by

$$\frac{dx_1}{dy_j},\ \frac{dx_2}{dy_j},\ \ldots\ldots\ \frac{dx_n}{dy_j},$$

the sum of the first members reduces itself by virtue of the equations (1.), (2.), to $\frac{dx_j}{dy_i}$, whilst the second side consists of the single term $\frac{dx_i}{dy_j}$. We have then

$$\frac{dx_i}{dy_j}=\frac{dx_j}{dy_i},$$

or, in other words, *if* $x_1, x_2, \ldots x_n$ *be found from the system of equations* (5.) *in terms of* $y_1, y_2, \ldots y_n$, *the resulting expressions are the partial differential coefficients of a certain function of* $y_1, y_2, \ldots, y_n$, *so that the system inverse to* (5.) *is of the form*

$$x_1=\frac{dY}{dy_1},\ x_2=\frac{dY}{dy_2},\ \ldots,\ x_n=\frac{dY}{dy_n}. \quad \ldots\ldots\ldots \quad (6.)$$

The relation between X and Y is easily found as follows. The equations (5.) and (6.) give

$$dX=y_1dx_1+y_2dx_2+\ldots+y_ndx_n$$

$$dY=x_1dy_1+x_2dy_2+\ldots+x_ndy_n;$$

whence, by addition, $$d(X+Y)=d(x_1y_1+x_2y_2+\ldots+x_ny_n),$$

and therefore $$X+Y=x_1y_1+x_2y_2+\ldots+x_ny_n \quad \ldots\ldots\ldots \quad (7.)$$

(omitting the arbitrary constant, which might of course be added).

The actual value of Y will then be

$$Y=-(X)+(x_1)y_1+(x_2)y_2+\ldots+(x_n)y_n, \quad \ldots\ldots \quad (8.)$$

in which the brackets indicate that $x_1, x_2, \ldots x_n$ are to be expressed in terms of $y_1, y_2, \ldots y_m$ so that Y may be a function of the latter variables only. It is easy to show *à posteriori* that the expression (8.) verifies the equations (6.), but I pass on to some further considerations. (See note at the end of Section II.)

3. Suppose the function X involves explicitly, besides the variables x_1, x_2, &c., any other quantity p, so that the expressions (x_1), (x_2), &c. (or the values of $x_1, x_2, \ldots$ in terms of y_1, y_2, &c.) will also involve p explicitly, and we shall have

$$\frac{d(\mathrm{X})}{dp}=\frac{d\mathrm{X}}{dp}+\frac{d\mathrm{X}}{dx_1}\frac{d(x_1)}{dp}+\frac{d\mathrm{X}}{dx_2}\frac{d(x_2)}{dp}+\ldots$$

$$=\frac{d\mathrm{X}}{dp}+y_1\frac{d(x_1)}{dp}+y_2\frac{d(x_2)}{dp}+\ldots$$

Now, differentiating the equation (8.) with respect to p (so far as it contains p *explicitly*), we obtain

$$\frac{d\mathrm{Y}}{dp}=-\frac{d(\mathrm{X})}{dp}+y_1\frac{d(x_1)}{dp}+y_2\frac{d(x_2)}{dp}+\ldots$$

which the equation above written reduces simply to

$$\frac{d\mathrm{X}}{dp}+\frac{d\mathrm{Y}}{dp}=0. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9.)$$

In the particular case in which X is a homogeneous function of $x_1, x_2, \ldots x_n$, and of m dimensions with respect to those variables, the equations (8.) and (9.) become

$$\left.\begin{aligned}&\mathrm{Y}=(m-1)(\mathrm{X})\\&\frac{d\mathrm{X}}{dp}+(m-1)\frac{d(\mathrm{X})}{dp}=0\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (10.)$$

and it is easily seen that Y is also homogeneous and of $\frac{m}{m-1}$ dimensions in $y_1, y_2, \ldots y_n$.

4. The theorems (8.) and (9.) are cases of more general ones which are easily proved in a perfectly similar way, and which I shall therefore only enunciate. If, by means of the equations (5.), art. 2, we express a set of n out of the $2n$ variables, consisting of r x's and $n-r$ y's, of which no two indices are the same, for example,

$$x_1, x_2, \ldots x_r, y_{r+1}, \ldots, y_n \quad \ldots\ldots\ldots\ldots \quad (\alpha.)$$

in terms of the remaining n variables,

$$y_1, y_2, \ldots y_r, x_{r+1}, \ldots, x_n; \quad \ldots\ldots\ldots\ldots \quad (\beta.)$$

then, taking $\mathrm{Q}=-(\mathrm{X})+(x_1)y_1+(x_2)y_2+\ldots+(x_r)y_r$

(in which the brackets indicate that the variables of the set $(\alpha.)$ are to be expressed in terms of those of the set $(\beta.)$, so that Q is a function of the latter set), we shall have

$$\frac{d\mathrm{Q}}{dy_i}=x_i \text{ from } i=0 \text{ to } i=r,$$

$$\frac{d\mathrm{Q}}{dx_j}=-y_j \text{ from } j=r+1 \text{ to } j=n,$$

and $$\frac{dX}{dp}+\frac{dQ}{dp}=0, \text{ as before*};$$

but the equations corresponding to (10.) will not subsist unless X be homogeneous with respect to the r variables $x_1, x_2, \ldots x_r$.

5. Let us now suppose that the function X contains, explicitly, besides the n variables $x_1, x_2, \ldots x_n$, another variable t, and also n constants $a_1, a_2, \ldots a_n$; and that these last are contained in such a way that the n equations

$$\frac{dX}{da_1}=b_1, \frac{dX}{da_2}=b_2, \ldots \frac{dX}{da_n}=b_n \quad \ldots\ldots\ldots\ldots \quad (11.)$$

would be algebraically sufficient to determine $a_1, a_2, \ldots a_n$ in terms of b_1, b_2, &c., x_1, &c. Then taking $$X_b=-(X)+(a_1)b_1+(a_2)b_2+\ldots+(a_n)b_n$$

(the brackets indicating that a_1, a_2, &c. are to be expressed as above supposed), we shall have, by the theorems of arts. 2 and 3,

$$\frac{dX_b}{db_1}=a_1, \frac{dX_b}{db_2}=a_2, \ldots. \frac{dX_b}{db_n}=a_n; \quad \ldots\ldots\ldots \quad (12.)$$

and also, for all values of i,

$$\frac{dX_b}{dx_i}=-\frac{dX}{dx_i}=-y_i; \quad \ldots\ldots\ldots\ldots\ldots \quad (13.)$$

to which we may add

$$\frac{dX_b}{dt}=-\frac{dX}{dt}=\frac{dY}{dt} \quad \ldots\ldots\ldots\ldots\ldots \quad (14.)$$

Now assuming the $2n$ equations (5.) and (11.), namely (for all values of i),

$$\frac{dX}{dx_i}=y_i, \frac{dX}{da_i}=b_i,$$

we may suppose each of the $2n$ variables $x_1, x_2, \ldots y_1, y_2, \ldots.$ to be expressed by means of them as a function of the $2n$ constants a_1, &c., b_1, &c., and t; or, conversely, each of the $2n$ constants to be expressed as a function of the variables x_1, &c., y_1, &c., and t. On the former hypothesis each of the variables $x_1, \ldots y_1, \ldots.$ is given as an explicit, and on the latter as an implicit function of the single variable t, which we will consider as independent; and *total differentiation with respect to* t will throughout this paper be denoted by *accents*, which will be used for no other purpose. Thus, p being any function of all the variables, we shall have

$$p'=\frac{dp}{dt}+\frac{dp}{dx_1}x_1'+\ldots+\frac{dp}{dy_1}y_1'+\ldots$$

For the rest, we may, when necessary, distinguish the meanings of the various partial

* Although these theorems, as stated in the text, are more general in form than those of the preceding article, they may, under another point of view, be considered as particular cases of them, and may in this way be best established.

differential coefficients employed, by referring to the hypotheses on which they are taken, and which I shall denote as follows:—

Hyp. I.—The $2n$ variables $x_1, x_2, \ldots y_1, y_2, \ldots$ expressed as functions of $a_1, a_2, \ldots b_1, b_2, \ldots$ and t.

Hyp. II.—The $2n$ constants $a_1, a_2, \ldots b_1, b_2, \ldots$ expressed as functions of $x_1, x_2, \ldots y_1, y_2, \ldots$ and t.

Hyp. III.—The n variables $y_1, y_2, \ldots y_n$ expressed as functions of the n variables $x_1, x_2, \ldots x_n$, the n constants $a_1, a_2, \ldots a_n$, and t (as by equations (5.)).

Hyp. IV.—The n constants $b_1, b_2, \ldots b_n$ expressed as functions of the n variables $x_1, \ldots x_n$, the n constants $a_1, \ldots a_n$, and t (as by equations (11.)).

6. Differentiating totally the equation (11.),

$$\frac{d\mathrm{X}}{da_i}=b_i$$

with respect to t, we obtain (observing that $\frac{d^2\mathrm{X}}{da_i dx_j}=\frac{dy_j}{da_i}$ by virtue of the conditions (5.)),

$$\frac{d^2\mathrm{X}}{da_i dt}+\frac{dy_1}{da_i}x_1'+\frac{dy_2}{da_i}x_2'+\ldots+\frac{dy_n}{da_i}x_n'=0$$

$\left(\text{where } \frac{dy_1}{da_i}, \text{ \&c. are taken on } \textit{Hyp.} \text{ III., art. 5.}\right)$.

Now let (Z) be a function of $x_1, \ldots x_n, t, a_1, \ldots a_n$, defined by the equation

$$(\mathrm{Z})=-\frac{d\mathrm{X}}{dt}, \quad \ldots \ldots \ldots \ldots \quad (15.)$$

the above equation then becomes

$$\frac{d(\mathrm{Z})}{da_i}=\frac{dy_1}{da_i}x_1'+\frac{dy_2}{da_i}x_2'+\ldots+\frac{dy_n}{da_i}x_n'.$$

If this equation be multiplied by $\frac{da_i}{dy_j}$, and the result on each side summed with respect to i, it will be seen that the coefficients of x_1', x_2', &c. on the second side all vanish except that of x_j', which reduces itself to 1 (see art. 1, equations (1.) (2.)); so that we have

$$\frac{d(\mathrm{Z})}{da_1}\frac{da_1}{dy_j}+\frac{d(\mathrm{Z})}{da_2}\frac{da_2}{dy_j}+\ldots+\frac{d(\mathrm{Z})}{da_n}\frac{da_n}{dy_j}=x_j'.$$

Now the expression on the left of this equation is equivalent to

$$\frac{d\mathrm{Z}}{dy_j},$$

if by Z (without brackets) we denote the result of substituting for $a_1, a_2, \ldots a_n$ in (Z), their values in terms of all the variables (*Hyp.* II.), so that Z is a function of the *variables only*. We have then, finally (writing i instead of j),

$$x_i'=\frac{d\mathrm{Z}}{dy_i}. \quad \ldots \ldots \ldots \ldots \quad (16.)$$

Again, we have (*Hyp.* III.) $\quad y_i'=\frac{dy_i}{dt}+\frac{dy_i}{dx_1}x_1'+\frac{dy_i}{dx_2}x_2'+\ldots.$

which, by (5.), (15.) and (16.), becomes

$$y_i' + \frac{d(Z)}{dx_i} = \frac{dZ}{dy_1}\frac{dy_1}{dx_1} + \frac{dZ}{dy_2}\frac{dy_2}{dx_2} + \ldots;$$

but it is plain that $\frac{d(Z)}{dx_i} = \frac{dZ}{dx_i} + \frac{dZ}{dy_1}\frac{dy_1}{dx_i} + \frac{dZ}{dy_2}\frac{dy_2}{dx_i} + \ldots$

(since (Z) would be derived from Z by substituting in the latter the expressions for $y_1, y_2, \ldots$ *Hyp.* III.). And since $\frac{dy_1}{dx_i} = \frac{dy_i}{dx_1}$, &c., comparing the two equations last written, we obtain

$$y_i' = -\frac{dZ}{dx_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (17.)$$

The system of $2n$ equations (16.) and (17.) express the result of eliminating the $2n$ constants from the equations (5.) and (11.) and their differential coefficients with respect to t. In other words, (16.) and (17.) are a system of $2n$ simultaneous differential equations of the first order, of which (5.) and (11.), or again, the equations supposed in *Hyp.* I. or II., art. 5, are the $2n$ integrals.

7. There are other remarkable relations between the partial differential coefficients of the expressions supposed in *Hyp.* I. and II., art. 5. For if we differentiate the equation $\frac{dX}{da_i} = b_i$ with respect to a_j (*Hyp.* I.), we obtain

$$\frac{d^2X}{da_i da_j} + \frac{d^2X}{da_i dx_1}\frac{dx_1}{da_j} + \frac{d^2X}{da_i dx_2}\frac{dx_2}{da_j} + \ldots = 0, \quad \ldots\ldots\ldots \quad (a.)$$

which gives, putting b_j for $\frac{dX}{da_j}$ and y_i for $\frac{dX}{dx_i}$,

$$\frac{db_j}{da_i} + \frac{dy_1}{da_i}\frac{dx_1}{da_j} + \frac{dy_2}{da_i}\frac{dx_2}{da_j} + \ldots + \frac{dy_n}{da_i}\frac{dx_n}{da_j} = 0 \quad \ldots\ldots\ldots \quad (b.)$$

$\left(\text{where } \frac{db_j}{da_i} \text{ refers to } \textit{Hyp.}\text{ IV., } \frac{dy_1}{da_i}\text{, &c. to } \textit{Hyp.}\text{ III., and } \frac{dx_1}{da_j}\text{, &c. to } \textit{Hyp.}\text{ I.}\right)$.

If then this equation be multiplied by $\frac{da_i}{dy_k}$ (*Hyp.* II.) and the result summed with respect to i, the sum of the first terms is $\frac{db_j}{dy_k}$ (*Hyp.* II.), and for the rest, the coefficient of $\frac{dx_k}{da_j}$ reduces itself to unity, whilst those of the remaining terms vanish (art. 1, equ. (1.), (2.)). Thus we have

$$\frac{db_j}{dy_k} = -\frac{dx_k}{da_j} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (18.)$$

(where the first side refers to *Hyp.* II., and the second to *Hyp.* I.).

Now if we treat the equations

$$\frac{dY}{dy_i} = x_i, \quad \frac{dY}{da_i} = -b_i$$

(see equations (6.) and (9.), putting a_i for p in the latter) exactly in the same way, it is plain that the result may be deduced from (18.) by interchanging x and y, and changing the sign of δ; thus

$$\frac{db_j}{dx_k}=\frac{dy_k}{da_j}.$$

Lastly, from the equations

$$\frac{dX_b}{db_i}=a_i, \quad \frac{dX_b}{dx_i}=-y_i \text{ (see (12.) and (13.))},$$

we should find in a similar manner

$$\frac{da_j}{dy_k}=\frac{dx_k}{db_j};$$

and from the analogous equations (the existence of which is obvious)

$$\frac{dY_b}{dy_i}=-x_i, \quad \frac{dY_b}{db_i}=-a_i$$

we should obtain

$$\frac{da_j}{dx_k}=-\frac{dy_k}{db_j}.$$

Collecting these results, and changing the indices, we have the system

$$\left.\begin{aligned} &\frac{dx_i}{da_j}=-\frac{db_j}{dy_i}, \quad \frac{dx_i}{db_j}=\frac{da_j}{dy_i} \\ &\frac{dy_i}{da_j}=\frac{db_j}{dx_i}, \quad \frac{dy_i}{db_j}=-\frac{da_j}{dx_i} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (19.)$$

in each of which equations the first member refers to *Hyp.* I., and the second to *Hyp.* II. (art. 5.); and it is to be remembered that there is no relation between the indices of the variables and those of the constants, so that the case of $i=j$ has no peculiarity*.

8. Let δ, Δ be symbols denoting two distinct sets of arbitrary and independent variations attributed to the $2n$ constants; then the equations

$$\frac{dX}{dx_i}=y_i, \quad \frac{dX}{da_i}=b_i$$

give

$$\delta X=\Sigma_i(y_i\delta x_i+a_i\delta b_i);$$

and if the operation Δ be performed on each side, we have

$$\Delta\delta X=\Sigma_i(\Delta y_i\delta x_i+\Delta a_i\delta b_i)+\Sigma_i(y_i\Delta\delta x_i+a_i\Delta\delta b_i).$$

* It is remarkable that each of the equations (19.) is also true on a different and separate hypothesis, as is apparent on inspection of the four different sets of equations,

$$\frac{dX}{dx_i}=y_i, \quad \frac{dX_b}{dx_i}=-y_i, \quad \frac{dY}{dy_i}=x_i, \quad \frac{dY_b}{dy_i}=-x_i$$

$$\frac{dX}{da_i}=b_i, \quad \frac{dX_b}{db_i}=a_i, \quad \frac{dY}{da_i}=-b_i, \quad \frac{dY_b}{db_i}=-a_i$$

(see the preceding articles).

If from this we subtract the corresponding equation obtained by inverting the order of the operations Δ, δ, remembering that $\Delta\delta u = \delta\Delta u$, we obtain

$$\Sigma_i(\delta x_i \Delta y_i - \Delta x_i \delta y_i) + \Sigma_i(\delta a_i \Delta b_i - \Delta a_i \delta b_i) = 0^* \quad . \quad . \quad . \quad . \quad . \quad . \quad (20.)$$

(The use here made of the double operation $\Delta\delta$, is due in principle to Mr. Boole. See his demonstration of a well-known theorem of Lagrange, of which the equation (20.) is a more general form†).

If in this equation we suppose δx_i, δy_i, &c. to be expressed in terms of δa_i, δb_i, &c. (*Hyp.* I.), and Δa_i, Δb_i, &c. in terms of Δx_i, Δy_i &c. (*Hyp.* II.), and compare the terms on the two sides, it is easy to derive the relations (19.). I preferred however to deduce them by a more direct method.

9. If x_i be expressed in terms of the $2n$ constants and t (*Hyp.* I.), and then each constant be expressed in terms of the variables (*Hyp.* II.), the result is an identical equation. Differentiating then with respect to x_j, y_k, we obtain the three equations

$$1 = \frac{dx_i}{da_1}\frac{da_1}{dx_i} + \frac{dx_i}{db_1}\frac{db_1}{dx_i} + \frac{dx_i}{da_2}\frac{da_2}{dx_i} + \frac{dx_i}{db_2}\frac{db_2}{dx_i} + \text{ &c.}$$

$$0 = \frac{dx_i}{da_1}\frac{da_1}{dx_j} + \frac{dx_i}{db_1}\frac{db_1}{dx_j} + \frac{dx_i}{da_2}\frac{da_2}{dx_j} + \frac{dx_i}{db_2}\frac{db_2}{dx_j} + \text{ &c.}$$

$$0 = \frac{dx_i}{da_1}\frac{da_1}{dy_k} + \frac{dx_i}{db_1}\frac{db_1}{dy_k} + \frac{dx_i}{da_2}\frac{da_2}{dy_k} + \frac{dx_i}{db_2}\frac{db_2}{dy_k} + \text{ &c.}$$

Three similar equations may be obtained by treating y_i in the same way. And if we apply to these six equations the transformations given by the system (19.), art. 7, the resulting theorems may be comprehended in the following statement.

If p, q be any two of the $2n$ variables $x_1, \ldots x_n, y_1, \ldots y_n$, then

$$\Sigma_i\left(\frac{dp}{db_i}\frac{dq}{da_i} - \frac{dp}{da_i}\frac{dq}{db_i}\right) = \Sigma_i\left(\frac{db_i}{dp}\frac{da_i}{dq} - \frac{db_i}{dq}\frac{da_i}{dp}\right) = \pm 1, \text{ or } = 0, \quad . \quad . \quad . \quad . \quad (21.)$$

according as p and q are or are not a *conjugate pair*, *i. e.* a pair of the form x_j, y_j. (The value $+1$ belongs to the case in which $p = x_j$, $q = y_j$, and -1 to the converse.)

Here p and q are a determinate pair of variables, and the summation refers to the constants, extending to the n *conjugate pairs*.

More important however are the converse theorems obtained in a perfectly similar way by expressing a_i, or b_i in terms of the variables (*Hyp.* II.), and supposing the variables to be again expressed in terms of the constants and t (*Hyp.* I.). Differentiating the resulting identical equation with respect to a_i, a_j, b_i, b_j, and applying the transformations (19.) as before, we have, putting h, k for a determinate pair of constants,

$$\Sigma_i\left(\frac{dh}{dy_i}\frac{dk}{dx_i} - \frac{dh}{dx_i}\frac{dk}{dy_i}\right) = \Sigma_i\left(\frac{dy_i}{dh}\frac{dx_i}{dk} - \frac{dx_i}{dh}\frac{dy_i}{dk}\right) = \pm 1, \text{ or } = 0 \quad . \quad . \quad . \quad . \quad (22.)$$

* This might be written

$$\Sigma_i \delta(x_i, y_i) + \Sigma_i \delta(a_i, b_i) = 0.$$

See the notation proposed in art. 1.

† Cambridge Mathematical Journal, vol. ii. p. 100.

according as h, k are or are not a *conjugate pair*, i. e. of the form a_j, b_j. (The value $+1$ belongs to $h=a_j$, $k=b_j$, and -1 to the converse.)

According to the notation proposed at the beginning of this paper, the above formula may be written

$$\Sigma_i \frac{d(h, k)}{d(y_i, x_i)} = \Sigma_i \frac{d(y_i, x_i)}{d(h, k)} = \pm 1, \text{ or } = 0.$$

By a usual and convenient abbreviation, the sum

$$\Sigma_i \frac{d(h, k)}{d(y_i, x_i)}$$

may be denoted by the symbol* $[h, k]$. We have then, by (22.),

$$[a_i, b_i] = -[b_i, a_i] = 1 \qquad [a_i, b_j] = [a_i, a_j] = [b_i, b_j] = 0, \quad . \quad . \quad . \quad . \quad . \quad (23.)$$

j being different from i; and, obviously,

$$[a_i, a_i] = [b_i, b_i] = 0.$$

Now let f, g be any two functions whatever of the $2n$ constants a_1, &c. b_1, &c.; when the latter are expressed in terms of the variables (*Hyp.* II.), f, g become also functions of the variables; and if h, k represent, as above, any pair whatever of a_1, &c., b_1, &c., we have (see art. 1.)

$$\frac{d(f, g)}{d(y_i, x_i)} = \Sigma \left\{ \frac{d(f, g)}{d(h, k)} \cdot \frac{d(h, k)}{d(y_i, x_i)} \right\},$$

the summation referring to h, k, and extending to every binary combination.

If, now, we sum each side of this equation *with respect to* i, we obtain

$$[f, g] = \Sigma \left\{ [h, k] \cdot \frac{d(f, g)}{d(h, k)} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24.)$$

(the summation referring as before to h, k). But, by (23.), $[h, k]$ is 0 unless h, k be a conjugate pair, and then it is ± 1; so that (24.) becomes simply

$$[f, g] = \Sigma_i \frac{d(f, g)}{d(a_i, b_i)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25.)$$

an equation which, written at length in the common notation, is

$$\Sigma_i \left(\frac{df}{dy_i} \frac{dg}{dx_i} - \frac{df}{dx_i} \frac{dg}{dy_i} \right) = \Sigma_i \left(\frac{df}{da_i} \frac{dg}{db_i} - \frac{df}{db_i} \frac{dg}{da_i} \right).$$

The expression on the right being a function of the constants a_1, &c., b_1, &c. only, the equation (25.) expresses obviously the following theorem.

If
$$f = \varphi(x_1, x_2, \ldots x_n, y_1, y_2, \ldots y_n, t)$$
$$g = \psi(x_1, x_2, \ldots x_n, y_1, y_2, \ldots y_n, t)$$

be any two integrals of the system of simultaneous equations (16.), (17.), art. 6, then

* Poisson employs the notation (h, k), which would have led to confusion if adopted here. Lagrange (in the *Méc. Anal.*) uses $[h, k]$, but with a different signification. See below, note to art. 34.

the expression $[f, g]$, or

$$\Sigma_i\left\{\frac{d\varphi}{dy_i}\frac{d\psi}{dx_i}-\frac{d\varphi}{dx_i}\frac{d\psi}{dy_i}\right\},$$

is constant; *i. e.* it becomes a function of the arbitrary constants only, if for x_i, &c., y_i, &c. be substituted their values in terms of the constants and t.

In the case in which (16.) and (17.) represent the dynamical equations, this is identical with the remarkable theorem discovered by Poisson. We shall have occasion to return to it presently.

10. If we treat the equations (21.) of the last article exactly in the same way as we have treated (22.), putting u, v for any two functions whatever of the $2n$ variables

$$x_1, x_2, \ldots x_n, y_1, y_2, \ldots y_n,$$

we find

$$\Sigma_i\frac{d(u, v)}{d(b_i, a_i)}=\Sigma_i\frac{d(u, v)}{d(x_i, y_i)},$$

and comparing this with the theorem (25.) of the last article, we see that both may be included in the following general enunciation:—

If u, v be either (1) any two functions whatever of the $2n$ constants a_1, &c., b_1, &c., or (2) any two functions whatever of the $2n$ variables x_1, &c., y_1, &c. (not containing t explicitly), then

$$\Sigma_i\left\{\frac{du}{dy_i}\frac{dv}{dx_i}-\frac{du}{dx_i}\frac{dv}{dy_i}+\frac{du}{db_i}\frac{dv}{da_i}-\frac{du}{da_i}\frac{dv}{db_i}\right\}=0,$$

or

$$\Sigma_i\left\{\frac{d(u, v)}{d(y_i, x_i)}+\frac{d(u, v)}{d(b_i, a_i)}\right\}=0. \quad \ldots\ldots\ldots\ldots \quad (26.)$$

(When u, v represent functions of the constants, the differential coefficients in the first term are taken on *Hyp.* II.; and, when functions of the variables, those in the second term on *Hyp.* I. (art. 5.)).

This property depends, as will be seen, solely on the relations (5.), (11.), arts. 2, 5, which are the only assumptions that have been made in deducing all the preceding propositions.

11. There are similar theorems in which the summation refers to the *numerators* of the differential coefficients; but as these are less remarkable, and moreover are deducible immediately from the equation (20.), art. 8, I shall omit them.

12. *Theorem.*—I proceed now to establish a theorem which may be considered as the converse of that expressed by (23.), art. 9.

Let $x_1, x_2, \ldots x_n, y_1, y_2, \ldots y_n$ be $2n$ variables, concerning which no supposition whatever is made, except that they are connected by n equations

$$\left.\begin{aligned} a_1&=\varphi_1(x_1, x_2, \ldots x_n, y_1, y_2, \ldots y_n)\\ a_2&=\varphi_2(x_1, x_2, \ldots x_n, y_1, y_2, \ldots y_n)\\ &\ldots\ldots\ldots\ldots\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (a.)$$

$a_1, a_2, \ldots a_n$ being n constants. The functions on the right may involve explicitly any

other quantities whatever, except a_1, &c. It is assumed that these equations are algebraically sufficient to determine each of the n variables $y_1, \ldots y_n$, as a function of the other n variables $x_1, \ldots x_n$ and the constants. Then the theorem in question is as follows:—

If, by means of the equations (a.), the n variables $y_1, \ldots y_n$ be expressed as functions of x_1, &c., then in order that the conditions

$$\frac{dy_i}{dx_j}=\frac{dy_j}{dx_i}$$

may subsist identically, it is necessary and sufficient that the expression $[a_i, a_j]$ (defined as in art. 9.) shall vanish for every binary combination of the n equations. This may be proved as follows:—

Putting h, k for any two of the constants a_1, a_2, &c., let $h=\varphi(x_1, \&c., y_1, \&c.)$ represent one of the equations (a.) above written. If in this equation the values of $y_1, \ldots y_n$ be expressed, as above supposed, in terms of x_1, &c., a_1, &c., it becomes identical. Differentiating it, on this hypothesis, with respect to x_i, we obtain

$$\frac{dh}{dx_i}+\frac{dh}{dy_1}\frac{dy_1}{dx_i}+\frac{dh}{dy_2}\frac{dy_2}{dx_i}+\ldots+\frac{dh}{dy_n}\frac{dy_n}{dx_i}=0;$$

and in like manner

$$\frac{dk}{dx_i}+\frac{dk}{dy_1}\frac{dy_1}{dx_i}+\frac{dk}{dy_2}\frac{dy_2}{dx_i}+\ldots+\frac{dk}{dy_n}\frac{dy_n}{dx_i}=0;$$

and if we multiply the first of these equations by $\frac{dk}{dy_i}$ and the second by $\frac{dh}{dy_i}$ and subtract, there results an equation which may be written as follows:—

$$\frac{dh}{dy_i}\frac{dk}{dx_i}-\frac{dh}{dx_i}\frac{dk}{dy_i}=\Sigma_j\left\{\frac{dy_j}{dx_i}\left(\frac{dh}{dy_j}\frac{dk}{dy_i}-\frac{dh}{dy_i}\frac{dk}{dy_j}\right)\right\};$$

or, putting now a_p, a_q instead of h, k, and employing the same notation as before,

$$\frac{d(a_p, a_q)}{d(y_i, x_i)}=\Sigma_j\left\{\frac{dy_j}{dx_i}\frac{d(a_p, a_q)}{d(y_j, y_i)}\right\}.$$

If now the terms on each side be summed with respect to i, the result on the first side is $[a_p, a_q]$; and observing that on the second side the term multiplied by $\frac{dy_i}{dx_j}$ will only differ in *sign* from that multiplied by $\frac{dy_j}{dx_i}$, we shall have

$$[a_p, a_q]=\Sigma_i\Sigma_j\left\{\left(\frac{dy_j}{dx_i}-\frac{dy_i}{dx_j}\right)\frac{d(a_p, a_q)}{d(y_j, y_i)}\right\} \quad \ldots\ldots\ldots \quad (27.)$$

the summation on the right extending to all binary combinations i, j. Suppose this equation to be written at length, and then after multiplying each side by

$$\frac{d(y_r, y_s)}{d(a_p, a_q)},$$

let the sum be taken with respect to all the binary combinations p, q. It follows

from the theorems of art. 1, that the coefficient of

$$\frac{dy_r}{dx_s}-\frac{dy_s}{dx_r}$$

on the right will reduce itself to unity, and that of each of the remaining terms to zero; so that we shall have, writing now j, i for r, s,

$$\frac{dy_j}{dx_i}-\frac{dy_i}{dx_j}=\Sigma_p\Sigma_q\left\{[a_p, a_q]\cdot\frac{d(y_j, y_i)}{d(a_p, a_q)}\right\}. \quad \ldots\ldots\ldots \quad (28.)$$

In order then that the expression $\frac{dy_j}{dx_i}-\frac{dy_i}{dx_j}$ should vanish identically for every binary combination of indices, it follows from (28.) that it is *sufficient*, and from (27.) that it is *necessary*, that each of the $\frac{n(n-1)}{2}$ terms $[a_p, a_q]$ should vanish, and *vice versâ*. It will be observed that the terms $[a_p, a_q]$ cannot vanish otherwise than identically, since they do not contain any of the constants a_1, a_2, &c., and it is by hypothesis impossible to eliminate all these constants from the equations (a.). It follows then that when the conditions $[a_p, a_q]=0$ subsist, the values of $y_1, \ldots y_n$ expressed as above, are identically the partial differential coefficients of a function of $x_1, \ldots x_n, a_1, \ldots a_n$.

We have thus established the theorem enunciated at the beginning of this article.

13. The preceding theorem may be made somewhat more general as follows:—

If we divide the $2n$ variables into any two sets of n each, so that no two in the same set are *conjugate* (as for instance

$$x_1, x_2, \ldots x_r, y_{r+1}, \ldots y_n$$
$$y_1, y_2, \ldots y_r, x_{r+1}, \ldots x_n),$$

and denote one set by

$$\xi_1, \xi_2, \ldots \xi_n,$$

and the other by

$$\pm\eta_1, \pm\eta_2, \ldots \pm\eta_n,$$

taking the + or − sign according as η_i represents y_i or x_i, it is obvious that the expression $\Sigma_i \frac{d(a_p, a_q)}{d(\eta_i, \xi_i)}$ is identical with $[a_p, a_q]$; and therefore whenever all the terms $[a_p, a_q]$ vanish, if the set $\eta_1, \eta_2, \ldots \eta_n$ can be expressed by means of the equations (a.) of the last article, in terms of $\xi_1, \xi_2, \ldots \xi_n, a_1, a_2, \ldots a_n$, their values will be the partial differential coefficients with respect to $\xi_1, \xi_2, \ldots \xi_n$, of a function of these variables and of the constants.

14. *Theorem.*—If of the system of $2n$ simultaneous differential equations of the first order

$$\left.\begin{aligned} x_1'=\frac{dZ}{dy_1}, \ \ldots, \ x_n'=\frac{dZ}{dy_n} \\ y_1'=-\frac{dZ}{dx_1}, \ \ldots, \ y_n'=-\frac{dZ}{dx_n} \end{aligned}\right\}. \quad \ldots\ldots\ldots \quad (I.)$$

(where Z denotes any function of $x_1, \ldots x_n, y_1, \ldots y_n$ and t, and accents denote as usual

total differentiation with respect to t) there be given n integrals, involving n arbitrary constants $a_1, \ldots a_n$, as

$$a_i = \varphi_i(x_1, x_2, \ldots x_n, y_1, y_2, \ldots y_n, t),$$

the remaining integrals may be found, whenever the $\frac{n(n-1)}{2}$ conditions $[a_i, a_j]=0$ are satisfied.

For let $y_1, y_2, \ldots y_n$ be expressed, by means of the given integrals, in terms of

$$x_1, \ldots x_n, a_1, \ldots a_n, t.$$

Their values so expressed will satisfy (art. 12.) the conditions

$$\frac{dy_j}{dx_i} - \frac{dy_i}{dx_j} = 0. \quad \ldots \quad (b.)$$

Let (Z) represent the result of substituting in Z these values of $y_1, \ldots, y_n$, so that (Z) is a given function of $x_1, \ldots x_n, a_1, \ldots a_n, t$. We shall have

$$\frac{d(\mathrm{Z})}{dx_i} = \frac{d\mathrm{Z}}{dx_i} + \frac{d\mathrm{Z}}{dy_1}\frac{dy_1}{dx_i} + \frac{d\mathrm{Z}}{dy_2}\frac{dy_2}{dx_i} + \ldots$$

which the equations (I.) and (b.) reduce to

$$\frac{d(\mathrm{Z})}{dx_i} = -y_i' + \frac{dy_i}{dx_1}x_1' + \frac{dy_i}{dx_2}x_2' + \ldots.$$

but

$$y_i' = \frac{dy_i}{dt} + \frac{dy_i}{dx_1}x_1' + \frac{dy_i}{dx_2}x_2' + \ldots.$$

consequently

$$\frac{d(\mathrm{Z})}{dx_i} = -\frac{dy_i}{dt}. \quad \ldots \quad (c.)$$

Looking now at the assemblage of equations (b.), (c.), we see that they express the following proposition:—

The values of

$$y_1, y_2, \ldots, y_n, -(\mathrm{Z}),$$

are the partial differential coefficients with respect to $x_1, x_2, \ldots x_n, t$, of one and the same function. Let this function be called X; we have then

$$\frac{d\mathrm{X}}{dx_i} = y_i, \quad \frac{d\mathrm{X}}{dt} = -(\mathrm{Z}); \quad \ldots \quad (\mathrm{II.})$$

and since $y_1, \ldots, y_n$, (Z) are given functions of x_1, &c., a_1, &c., t, the function X can be found by simple integration.

Let us then suppose X to be known, and let us take the total differential coefficient with respect to t, of $\frac{d\mathrm{X}}{da_i}$; we shall have

$$\left(\frac{d\mathrm{X}}{da_i}\right)' = \frac{d^2\mathrm{X}}{da_i dt} + \frac{d^2\mathrm{X}}{da_i dx_1}\cdot x_1' + \frac{d^2\mathrm{X}}{da_i dx_2}\cdot x_2' + \ldots.$$

which, by virtue of (I.) and (II.), becomes

$$\left(\frac{d\mathrm{X}}{da_i}\right)' = -\frac{d(\mathrm{Z})}{da_i} + \frac{d\mathrm{Z}}{dy_1}\frac{dy_1}{da_i} + \frac{d\mathrm{Z}}{dy_2}\frac{dy_2}{da_i} + \ldots$$

but $$\frac{d(Z)}{da_i}=\frac{dZ}{dy_1}\frac{dy_1}{da_i}+\frac{dZ}{dy_2}\frac{dy_2}{da_i}+\dots$$

(since (Z) is derived from Z by introducing the values of $y_1, \dots y_n$, in terms of x_1, &c., $a_1, \dots a_n$), hence the second member of the preceding equation vanishes, and we have

$$\left(\frac{dX}{da_i}\right)'=0,$$

so that $\frac{dX}{da_i}$ is constant, and we may write

$$\frac{dX}{da_i}=b_i, \quad \dots \quad \text{(III.)}$$

and b_i is an independent arbitrary constant, as it is easy to prove; it is however unnecessary to do so here, because we have in fact already proved it in showing that the elimination of $a_1, \dots a_n, b_1, \dots b_n$, from the system of equations (II.), (III.), leads to the differential equations (I.) (see art. 6.). The n equations (III.) give therefore the remaining n integrals of the system (I.), of which (II.) and (III.) together are the complete solution.

The system of equations (II.), (III.) being the same as that discussed in the preceding articles, all the conclusions there obtained will continue to subsist.

15. Suppose the expression for Z (see the last article) in terms of the variables is

$$Z=f(x_1, x_2, \dots x_n, y_1, y_2, \dots y_n, t),$$

Z is changed into (Z) by the substitution of $\frac{dX}{dx_1}$ for y_1, &c.; and since $\frac{dX}{dt}$ is (identically) $=-(Z)$, the equation

$$\frac{dX}{dt}+f\left(x_1, x_2, \dots x_n, \frac{dX}{dx_1}, \dots, \frac{dX}{dx_n}, t\right)=0 \quad \dots \quad \text{(X.)}$$

is a partial differential equation satisfied by the function X.

We have thus arrived, by an inverse route, at the point from which Sir W. Hamilton's theory, as improved by Jacobi, sets out.

Jacobi, namely, has shown (by a demonstration immediately applying only to a particular form of the equation (X.), but easily extended), that if X be *any "complete" solution* of the equation (X.), that is, a solution involving (besides the constant which may be merely added to X) n arbitrary constants $a_1, a_2, \dots a_n$, in such a way that they cannot be all eliminated from the $n+1$ equations obtained by differentiating X with respect to $x_1, \dots x_n, t$, without employing *all* those equations, then X possesses the properties of Sir W. Hamilton's "Principal Function," or in other words, gives all the integrals of the system (I.) by means of the system (II.), (III.). It will be desirable briefly to indicate the mode in which this demonstration may be made to apply to the general form (X.).

Assuming that a complete solution X, of that equation, is given, put $\frac{dX}{dx_i}=y_i$; then

differentiating the equation (X.) with respect to x_i, and employing the equations

$$\frac{dy_p}{dx_q}=\frac{dy_q}{dx_p},$$

we have

$$\frac{dy_i}{dt}+\frac{df}{dx_i}+\frac{df}{dy_1}\frac{dy_i}{dx_1}+\frac{df}{dy_2}\frac{dy_i}{dx_2}+\ldots=0\,;$$

on the other hand, taking the differential coefficient of y_i with respect to t, without assuming anything as to the nature of the relations between t and the other variables, we find

$$y_i'=\frac{dy_i}{dt}+\frac{dy_i}{dx_1}x_1'+\frac{dy_i}{dx_2}x_2'+\ldots.$$

and adding to this the preceding equation,

$$y_i'+\frac{df}{dx_i}=\frac{dy_i}{dx_1}\left(x_1'-\frac{df}{dy_1}\right)+\frac{dy_i}{dx_2}\left(x_2'-\frac{df}{dx_2}\right)+\ldots$$

from which it follows that the n assumptions

$$x_i'=\frac{df}{dy_i}$$

would involve the n further equations

$$y_i'=-\frac{df}{dx_i}.$$

Again, the n assumptions

$$\frac{dX}{da_i}=b_i$$

would give, by combining the n equations obtained by differentiating totally with respect to t, viz.

$$\frac{d^2X}{da_idt}+\frac{d^2X}{da_idx_1}x_1'+\frac{d^2X}{da_idx_2}x_2'+\ldots.=0,$$

with the n others obtained by differentiating the equation (X.) with respect to a_i, viz.

$$\frac{d^2X}{da_idt}+\frac{df}{dy_1}\frac{d^2X}{da_idx_1}+\frac{df}{dy_2}\frac{d^2X}{da_idx_2}+\ldots=0,$$

the n following, namely,

$$\frac{d^2X}{da_idx_1}\left(x_1'-\frac{df}{dy_1}\right)+\frac{d^2X}{da_idx_2}\left(x_2'-\frac{df}{dy_2}\right)+\ldots.=0,$$

from which it follows *either* that $x_i'=\frac{df}{dy_i}$, *or* that the determinant formed with the n^2 expressions $\frac{d^2X}{da_idx_j}$, or $\frac{d}{da_i}\left(\frac{dX}{dx_j}\right)$, vanishes; but this last condition would express, as is well known, the possibility of eliminating the n constants a_1, a_2, ... a_n from the n equations

$$\frac{dX}{dx_j}=\Psi_j(x_1,\ \&c.,\ a_1,\ \&c.,\ t),$$

which would contradict the assumption that X is a *complete* solution of the equation (X.).

Finally, then, if X be a complete solution, the assumptions $\frac{dX}{da_i}=b_i$ involve as a consequence the relations $x_i'=\frac{df}{dy_i}$, and these again involve $y_i'=-\frac{df}{dx_i}$, where y_i stands for $\frac{dX}{dx_i}$.

In thus applying JACOBI's demonstration I have slightly altered its form, in order to bring more prominently into view the necessity for X being a *complete* solution.

16. It is obvious, from the considerations given in art. 13, that instead of the equation (X.) of the last article, we might employ any one of the analogous equations obtained by distributing the variables as explained in the article referred to, and then writing $\frac{dQ}{d\xi_i}$ for η_i in the expression for Z. The function Q will be a "principal function." In particular, if we take the equation

$$\frac{dY}{dt}-f\left\{\frac{dY}{dy_1}, \frac{dY}{dy_2}, \ldots, y_1, y_2, \ldots y_n, t\right\}=0,$$

any complete solution will give the integrals of the differential equations (I.) by means of the system

$$\frac{dY}{dy_i}=x_i, \quad \frac{dY}{da_i}=b_i.$$

The whole number of partial differential equations from each of which a "principal function" can be obtained, will obviously be 2^n. The relations between these different principal functions will be apparent from the conclusions of art. 4*.

17. If $x_1, x_2, \ldots x_n$ represent all the independent coordinates (of whatever kind) in any ordinary dynamical problem, and T the expression for the *vis viva*† in terms of x_1, &c., x_1', &c., the equations of motion are, as is well known,

$$\left(\frac{dT}{dx_i'}\right)'-\frac{dT}{dx_i}=\frac{dU}{dx_i}, \quad \ldots\ldots\ldots\ldots \quad (T.)$$

where U is a function of $x_1, \ldots x_n$, which may also contain t explicitly, but not x_1', &c. LAGRANGE, to whom these formulæ are due, was also the first to employ the expressions $\frac{dT}{dx_i'}$ as new variables, instead of x_i'. But Sir W. HAMILTON first showed that this substitution $\left(\text{putting } \frac{dT}{dx_i'}=y_i\right)$ would reduce the n equations (T.) to the $2n$ equations of the first order of the form (I.), art. 14. His demonstration, however‡, depends upon the circumstance that T is, in dynamical problems, necessarily homogeneous with respect to $x_1', \ldots x_n'$, and I am not aware that any other case has hitherto been contemplated.

The investigations of the preceding articles will however enable us to apply a

* Compare Sir W. HAMILTON's expressions, Philosophical Transactions, 1835, p. 99, art. 5.

† I here adopt, what I hope will be universally adopted, the suggestion of CORIOLIS and Professor HELMHOLTZ, that the definition of *vis viva* should be *half* the sum of products of masses by squares of velocities.

‡ Philosophical Transactions, 1835, p. 97, art. 3.

similar transformation to the equations (T.), in the case in which no limitation is imposed upon the form of the function T, as I shall now proceed to show.

18. Putting $T+U=W$, we shall have (since U does not contain x_i', &c.)

$$\left(\frac{dW}{dx_i'}\right)'=\frac{dW}{dx_i}. \quad \ldots\ldots\ldots\ldots \quad (W.)$$

Let $\frac{dW}{dx_i'}=y_i$; then if we take

$$Z=-(W)+(x_1')y_1+(x_2')y_2+\ldots+(x_n')y_n \quad \ldots\ldots\ldots \quad (V.)$$

(where, in the terms enclosed in brackets, x_1', x_2', &c. are to be expressed in terms of y_1, y_2, &c., x_1, x_2, &c.), we shall have, by the theorems of the former articles (see equations (6.), (8.), (9.) of arts. 2 and 3, putting x_i' instead of x_i and x_i instead of p, in those equations),

$$x_i'=\frac{dZ}{dy_i}, \quad \ldots\ldots\ldots\ldots \quad (\alpha.)$$

and

$$\frac{dW}{dx_i}=-\frac{dZ}{dx_i},$$

so that the equation (W.) becomes

$$y_i=-\frac{dZ}{dx_i}, \quad \ldots\ldots\ldots\ldots \quad (\beta.)$$

and (α.), (β.) are of the form in question* ((I.), art. 14.). Thus, so far as the application of any methods of integration, founded upon the preceding principles, and the theories of Sir W. Hamilton and Jacobi, to the system (T.), art. 16, is concerned, there is no restriction to the form of the function T. This extension is probably at present of no practical importance, but may perhaps be thought of some interest in a purely analytical point of view.

19. Returning now to the suppositions and conclusions of art. 14, let us further suppose that Z does not contain t explicitly, so that

$$Z'=\Sigma_i\left(\frac{dZ}{dx_i}x_i'+\frac{dZ}{dy_i}y_i'\right)=0$$

by virtue of the system (I.); in this case

$$Z=h. \quad \ldots\ldots\ldots\ldots \quad (h.)$$

is one of the integrals of the system, and if we suppose this to be one of the n given integrals from which the principal function X is to be found, so that

$$h, a_1, a_2, \ldots a_{n-1}$$

are now the n arbitrary constants, and the conditions

$$[a_i, a_j]=0, \ [h, a_i]=0$$

subsist, it is plain that we shall have

$$(Z)=h,$$

* In the case in which T is homogeneous and of the second degree, in $x_1', x_2', \ldots x_n'$, it is obvious that the expression for Z reduces itself to $2(T)-W$, or $(T)-U$.

since the expression for Z must reduce itself identically to h when the values of $y_1 \dots y_n$ obtained from the integrals are substituted in it. Hence

$$\frac{dX}{dt} = -h,$$

and therefore $$X = -ht + V,$$

V being a function not containing t explicitly. We have then $\frac{dX}{dx_i} = \frac{dV}{dx_i}$, so that V is to be found from the n expressions

$$\frac{dV}{dx_i} = y_i.$$

Lastly, the n remaining integrals will be

$$\frac{dX}{dh} = \tau, \quad \frac{dX}{da_i} = b_i$$

(τ representing the arbitrary constant conjugate to h); and, substituting in these the above expression for X, we obtain

$$\frac{dV}{dh} = t + \tau, \quad \frac{dV}{da_i} = h_i. \quad \dots \quad (29.)$$

The function V now satisfies, and may be defined by, the partial differential equation

$$f\left(x_1, \dots x_n, \frac{dV}{dx_1}, \dots, \frac{dV}{dx_n}\right) = h, \quad \dots \quad (V.)$$

where $f(x_1, \dots x_n, y_1, \dots y_n)$ is the expression for Z in terms of the variables.

This, in dynamical problems, is the case in which the so-called "principle of *vis viva*" subsists. I shall, in the rest of this paper, use h exclusively in the above signification, and call it, whether actually referring to a dynamical problem or not, the "constant of *vis viva*," whilst the integral $Z = h$ may be called the "integral of *vis viva*."

20. When the $2n$ integrals of the system of differential equations (I.), art. 14, are expressed in the manner which has been explained, it follows from the conclusions of former articles, that when these integrals are put in the form

$$a_i = \varphi_i(x_1, \dots, x_n, y_1, \dots y_n, t)$$
$$b_i = \psi_i(x_1, \dots, x_n, y_1, \dots y_n, t),$$

the conditions $[a_i, b_i] = 1$, $[a_i, b_j] = 0$, $[b_i, b_j] = 0$ will subsist, as well as $[a_i, a_j] = 0$. I shall call any system of $2n$ integrals in which these conditions are fulfilled, a "normal solution," or a system of "normal integrals," whilst the $2n$ arbitrary constants contained in such a system may be called "normal elements." Any pair a_i, b_i may be called (as before) *conjugate* elements. In the case considered in art. 19, h and τ are conjugate elements, these letters being used instead of a, b, merely from obvious motives of convenience.

It has been one principal object of these investigations to ascertain what advantages could be gained—either for the actual integration of a system of equations of the

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form (I.), or for the transformation of known solutions into forms convenient for the application of the method of variation of elements—by making the discovery of principal functions depend upon that of n integrals satisfying given conditions, rather than upon the solution of a partial differential equation. Having now prepared the way for this inquiry, I shall proceed with it in the following section.

Section II.

21. *Theorem.*—If p, q, r be any three functions whatever of the $2n$ variables $x_1, \ldots, x_n, y_1, \ldots y_n$, then

$$[[p, q], r]+[[q, r], p]+[[r, p], q]=0. \quad . \quad . \quad . \quad . \quad . \quad (30.)$$

(The symbols have the same signification as in the last section. See art. 9.)

This may be proved as follows. It is evident that if the above expression were developed, each term would consist of a *second* differential coefficient of one of the functions p, q, r, multiplied by a *first* differential coefficient of each of the other two.

Consider then the terms in which p is twice differentiated; these will be of the three forms

$$\frac{d^2p}{dx_i dy_j}\cdot\frac{dq}{dx_j}\cdot\frac{dr}{dy_i}, \quad \frac{d^2p}{dx_i dx_j}\cdot\frac{dq}{dy_i}\cdot\frac{dr}{dy_j}, \quad \text{and} \quad \frac{d^2p}{dy_i dy_j}\cdot\frac{dq}{dx_i}\cdot\frac{dr}{dx_j},$$

each of which will arise from the first and third terms of (30.) only. (It is to be observed that i may $=j$.)

Now if we examine each of these forms, we see easily that for every term arising from the *first* term of (30.), there is a similar term with the *opposite sign* arising from the *third* term of (30.); and since a similar proposition would be true of the terms in which q, r, respectively, are twice differentiated, the whole expression on the left of the equation (30.) vanishes identically. The theorem is therefore established.

It is obvious that p, q, r may contain, explicitly, any other quantities (as t) besides the $2n$ variables with respect to which the differentiations are performed.

Let ξ represent, either, one of the $2n$ variables x_1, &c., y_1, &c., or any other quantity whatever, explicitly contained in p and q. It is evident that we shall have

$$\frac{d}{d\xi}[p, q]=\left[\frac{dp}{d\xi}, q\right]+\left[p, \frac{dq}{d\xi}\right]. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31.)$$

22. Resuming now the consideration of the $2n$ simultaneous differential equations discussed in the first section, namely,

$$x_i'=\frac{dZ}{dy_i}, \quad y_i'=-\frac{dZ}{dx_i}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

we shall be enabled, by means of the theorems (30.), (31.) of the last article, to give a very simple and direct proof of the proposition indirectly demonstrated in art. 9.

For let u be any function whatever of the variables x_1, &c., y_1, &c., t; then

$$u'=\frac{du}{dt}+\Sigma_i\left(\frac{du}{dx_i}x_i'+\frac{du}{dy_i}y_i'\right),$$

and if the values of x_i', y_i' given by (I.) be substituted in this expression, it becomes

$$u'=\frac{du}{dt}+[Z, u]. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32.)$$

Let $u=[p, q]$, then (making use of (31.))

$$[p, q]'=\left[\frac{dp}{dt}, q\right]+\left[p, \frac{dq}{dt}\right]+\Big[Z, [p, q]\Big].$$

Now suppose that, by virtue of the differential equations (I.), the values of p and q are constant; or, in other words, that

$$p=\varphi(x_1, \&c., y_1, \&c., t)$$
$$q=\psi(x_1, \&c., y_1, \&c., t)$$

are any two integrals whatever of the system (I.); p, q representing two arbitrary constants. The equation $p'=0$ gives (see (32.))

$$\frac{dp}{dt}+[Z, p]=0,$$

or

$$\frac{dp}{dt}=-[Z, p],$$

hence

$$\left[\frac{dp}{dt}, q\right]=-\Big[[Z, p], q\Big]=\Big[q, [Z, p]\Big].$$

In like manner

$$\left[p, \frac{dq}{dt}\right]=\Big[p, [q, Z]\Big].$$

Thus the expression given above for $[p, q]'$ becomes

$$[p, q]'=\Big[p, [q, Z]\Big]+\Big[q, [Z, p]\Big]+\Big[Z, [p, q]\Big],$$

which is identically equal to 0, by the theorem (30.). Consequently, for any two integrals p and q,

$$[p, q]=\text{constant}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33.)$$

This theorem, as has been already mentioned, was discovered, in the case of the dynamical equations, by Poisson; and the fact that he was able to arrive at it through so long and complex a process as that which he has given in his first memoir on the Variation of Arbitrary Constants*, must be looked upon as a remarkable instance of his analytical skill. I am not acquainted with any attempt to simplify the demonstration, except that of Sir W. Hamilton†; in fact it is probable that no material simplification was attainable without the help of the transformation of the differential equations to the form (I.), towards which Poisson (as Jacobi has remarked) only made a first step. Sir W. Hamilton's demonstration may certainly be considered simple as compared with that of Poisson. That which I have given above will, I hope, be regarded as a further improvement.

23. In what follows I shall use such expressions as "the integral c," as an abbreviation for "the equation $c=\varphi(x_1, \&c., y_1, \&c., t)$."

* Journ. de l'École Polytechnique, tom. viii.

† Philosophical Transactions, 1835, p. 108–9.

It is of course understood that the function on the right contains neither c nor any other arbitrary constant explicitly.

Let then f, g be any two given integrals of the system (I.). It has been shown that we shall always have

$$[f, g] = \text{constant}. \quad \ldots \quad (\text{K.})$$

But this equation may be true either (1) identically, or (2) not identically. In the first case the expression $[f, g]$ may either be identically $=0$, or it may reduce itself identically to a *determinate constant*, which might always be made unity by multiplying one of the integrals by a factor. (In the case of a "*normal system*" of integrals (art. 20.), it has been seen that every binary combination gives either 0 or 1.) But if the above equation (K.) be not identically true, so that $[f, g]$ obtains a constant value only by virtue of the differential equations, then the constant on the right of (K.) is an *arbitrary constant*, and that equation is itself an integral. But here again there are two cases; for the function $[f, g]$ may be only a combination of the functions on the right of the two integrals f, g; and then (K.) is not a new integral, but only a combination of the two given ones; or, on the other hand, $[f, g]$ may be a function independent of f, g; and then (K.) is really a new integral, which cannot be produced by merely combining the other two. Thus it appears that Poisson's theorem may in some cases *lead to the discovery of new integrals*, when two are known. On this subject, and others connected with it, I refer to the interesting memoir of M. Bertrand in Liouville's Journal (1852), "Sur l'intégration des équations différentielles de la Mécanique."

24. Let $c_1, c_2, \ldots c_m$ be any m integrals, and let f, g be any two functions of the m constants $c_1, c_2, \ldots, c_m$, so that f, g are also two integrals; and considering f, g as functions of $c_1, \ldots, c_m$, and, through them, of the variables, we have exactly as in art. 9, equation (24.),

$$[f, g] = \Sigma\left\{\frac{d(f, g)}{d(c_i, c_j)} \cdot [c_i, c_j]\right\}, \quad \ldots \quad (\text{L.})$$

the summation extending to all binary combinations of the m constants c_1, &c. If then we suppose $k_1, k_2, \ldots, k_m$ to be m functions (such as h, k) of the m constants $c_1, \ldots, c_m$, we shall have for any pair k_p, k_q,

$$[k_p, k_q] = \Sigma\left\{\frac{d(k_p, k_q)}{d(c_i, c_j)} \cdot [c_i, c_j]\right\} \quad \ldots \quad (34.)$$

(the summation referring as before to i, j); and the inverse equations (obtained either by considering c_1, &c. as functions of k_1, &c., and reasoning in the same way, or by multiplying the above equation by $\frac{d(c_r, c_s)}{d(k_p, k_q)}$ and summing with respect to p, q) will be

$$[c_i, c_j] = \Sigma\left\{\frac{d(c_i, c_j)}{d(k_p, k_q)} \cdot [k_p, k_q]\right\} \quad \ldots \quad (35.)$$

(the summation referring to p, q).

This inversion can only fail in the case in which the equations expressing k_1, &c. in

terms of c_1, &c. are not all independent; a supposition which we exclude, in order that $k_1, \ldots k_m$ may represent m distinct integrals.

The equations above written lead obviously to the following conclusions:—

(1.) If f be a given function of the m constants $c_1, \ldots c_m$; then the determination of another function g, such that $[f, g] = 0$, depends in general upon the solution of a linear partial differential equation of the first order.

(2.) It is impossible that the conditions $[k_i, k_j] = 0$ can exist for every binary combination of $k_1, \ldots, k_m$, unless $[c_i, c_j] = 0$ for every binary combination of $c_1, \ldots, c_m$.

25. As an illustration of the first of these conclusions, we may take a case which actually occurs in many dynamical problems. Let c_1, c_2, c_3 be three integrals, such that

$$[c_2, c_3] = c_1, \quad [c_3, c_1] = c_2, \quad [c_1, c_2] = c_3, \quad \ldots\ldots\ldots \quad (c.)$$

and let it be required to find a function g of c_1, c_2, c_3, such that $[c_1, g] = 0$. The equation (L.) of the last article gives, if we put $f = c_1$, and introduce the conditions $(c.)$,

$$c_3 \frac{dg}{dc_2} - c_2 \frac{dg}{dc_3} = 0.$$

The solution of which is

$$g = \psi(c_1^2 + c_2^2), \quad \ldots\ldots\ldots\ldots \quad (g.)$$

ψ being an arbitrary function (which may evidently also contain c_1 in an arbitrary manner).

If, instead of $f = c_1$, we put $f = \varphi(c_1^2 + c_2^2 + c_3^2)$, it will be found that the expression on the right of the equation (L.) vanishes identically; so that in this case, if g be any arbitrary function of c_1, c_2, c_3, the condition $[f, g] = 0$ will be satisfied.

26. If $a_1, a_2, \ldots a_n, b_1, b_2, \ldots b_n$ be a system of *normal* elements (art. 20.), we have (equation (25.), art. 9.)

$$[f, g] = \Sigma_i \frac{d(f, g)}{d(a_i, b_i)},$$

where f, g represent any two functions of the elements, or in other words, any two integrals whatever. If in the above equation we put successively $f = a_i$, $f = b_i$, we obtain

$$[a_i, g] = \frac{dg}{db_i}, \quad [b_i, g] = -\frac{dg}{da_i}. \quad \ldots\ldots\ldots\ldots \quad (36.)$$

In the case where the principle of *vis viva* subsists, we may suppose the constant of *vis viva*, h, to be one of the elements. In this case (see (29.), art. 19.) the element conjugate to h is τ, and t appears in none of the integrals explicitly, except one, namely, the integral conjugate to h, which is

$$\tau = -t + \frac{dV}{dh}.$$

If, then, g be any integral whatever, *not containing* t *explicitly*, it cannot contain τ, since any combination of the normal integrals involving τ, will involve it in the form

$\tau+t$. Consequently, for every such integral we shall have, by (36.),

$$[g, h]=0, \quad \ldots \ldots \ldots \ldots \quad (37.)$$

since $$\frac{dg}{d\tau}=0.$$

This particular consequence of the formula (36.) follows also immediately from (32.), art. 22, since the equation $g'=0$ gives, by (32.), $[Z, g]=0$, and in this case $Z=h$, so that $[Z, g]=[h, g]$. In this manner the theorem expressed by (37.) has been already obtained by M. BERTRAND.

Examples of the preceding Methods.

27. I shall now exemplify the principles which have been explained, by applying them to two of the most familiar as well as important problems of dynamics. First then let it be required to obtain in a normal form the integrals of the differential equations which determine the motion of a material point, acted on by a force emanating from a fixed centre and depending only on the distance.

Taking the centre of force as the origin of a system of rectangular coordinates, let m be the mass, and x, y, z the coordinates of the moving point. Then

$$T=\tfrac{1}{2}m(x'^2+y'^2+z'^2),$$

and U (see art. 17.) is a given function of r, say $\varphi(r)$, where $r^2=x^2+y^2+z^2$. Let us put

$$\frac{dT}{dx'}=u, \quad \frac{dT}{dy'}=v, \quad \frac{dT}{dz'}=w,$$

so that, referring to the notation used in the preceding pages, we have

$$x, y, z \text{ instead of } x_1, x_2, x_3$$

$$u, v, w \text{ instead of } y_1, y_2, y_3.$$

Moreover, $$u=mx', \quad v=my', \quad w=mz'.$$

Hence we obtain $$Z=(T)-U=m^{-1}(u^2+v^2+w^2)-\varphi(r),$$

so that the integral of *vis viva*, or $Z=h$, becomes

$$\frac{1}{m}(u^2+v^2+w^2)-\varphi(r)=h;$$

and the three integrals which express the conservation of areas become

$$yw-zv=c_1$$

$$zu-xw=c_2$$

$$xv-yu=c_3.$$

These integrals are immediately seen to satisfy the conditions

$$[c_2, c_3]=-c_1, \quad [c_3, c_1]=-c_2, \quad [c_1, c_2]=-c_3;$$

from which it follows (see art. 25, the result of which is obviously unaffected by the negative signs), that if we take $k=(c_1^2+c_2^2+c_3^2)^{\frac{1}{2}}$, the condition $[c_3, k]=0$ will be satisfied

(as is easily found to be true); and since neither of the integrals c_3, k contain t explicitly, the conditions $[h, c_3]=0$, $[h, k]=0$ will subsist also (art. 26.). Hence it follows that if we solved algebraically the three integrals h, c_3, k so as to express u, v, w in terms of x, y, z, their values would be the partial differential coefficients of a function V, from which the three remaining integrals could be found (arts. 12 and 19.).

But it is more convenient to adopt a different system of coordinates. Reverting then to the primitive form of the three integrals which we have chosen, and writing c instead of c_3, we have

$$T-U=h. \quad \text{(i.)}$$

$$m(xy'-yx')=c. \quad \text{(ii.)}$$

$$m^2(r^2(x'^2+y'^2+z'^2)-r^2r'^2)=k^2. \quad \text{(iii.)}$$

28. Let us now employ, instead of x, y, z, the three coordinates ϱ, θ, z; where z is the same as before, ϱ is the projection of r on the plane of xy, and θ is the angle between ϱ and the positive axis of x. We shall thus have

$$\varrho^2+z^2=r^2, \quad x=\varrho\cos\theta, \quad y=\varrho\sin\theta,$$

and

$$T=\tfrac{1}{2}m(\varrho'^2+\varrho^2\theta'^2+z'^2).$$

Let

$$\frac{dT}{d\varrho'}=u, \quad \frac{dT}{d\theta'}=v, \quad \frac{dT}{dz'}=w$$

(where u and v have now a new signification), then

$$\varrho'=\frac{u}{m}, \quad \theta'=\frac{v}{m\varrho^2}, \quad z'=\frac{w}{m};$$

and the three integrals at the end of the last article become, after obvious reductions,

$$\frac{1}{2m}\left(u^2+\frac{v^2}{\varrho^2}+w^2\right)=h+\varphi(r). \quad \text{(i.)}$$

$$v=c. \quad \text{(ii.)}$$

$$(\varrho w-zu)^2+\frac{r^2}{\varrho^2}v^2=k^2. \quad \text{(iii.)}$$

The conditions $[h, c]=0$, $[h, k]=0$, $[c, k]=0$ continue to subsist with reference to the new variables; the two former *necessarily*, because (ii.) and (iii.) do not contain t (art. 26.), and the third *actually*, as is seen on trial (*not accidentally*, as will be shown hereafter).

We know, therefore, that the values of u, v, w, found from these equations, will be the partial differential coefficients with respect to ϱ, θ, z of a function V of these latter variables.

The two first give

$$u^2+w^2=2m(h+\varphi(r))-\frac{c^2}{\varrho^2};$$

and if we multiply this by $\varrho^2+z^2=r^2$, and subtract (iii.), we obtain (introducing the condition (ii.)

$$(\varrho u+zw)^2=2mr^2(h+\varphi(r))-k^2.$$

Lastly, if this be combined with (iii.), the following expressions are found for u and w:

$$u=\frac{\varrho}{r^2}\left\{2mr^3(h+\varphi(r))-k^2\right\}^{\frac{1}{2}}-\frac{z}{r^2}\left\{k^2-\frac{r^2}{\varrho^2}c^2\right\}^{\frac{1}{2}}$$

$$w=\frac{z}{r^2}\left\{2mr^3(h+\varphi(r))-k^2\right\}^{\frac{1}{2}}+\frac{\varrho}{r^2}\left\{k^2-\frac{r^2}{\varrho^2}c^2\right\}^{\frac{1}{2}}$$

(in which it is to be remembered that $r^2=z^2+\varrho^2$), and if to these we join the equation (ii.), the values of u, v, w are explicitly given in terms of the conjugate variables ϱ, θ, z. We have then (art. 19.)

$$V=\int(ud\varrho+vd\theta+wdz);$$

or, substituting the above values,

$$V=c\theta+\int\left\{\frac{\varrho d\varrho+zdz}{r^2}(2mr^3(h+\varphi(r))-k^2)^{\frac{1}{2}}+\frac{\varrho dz-zd\varrho}{r^2}\left(k^2-\frac{r^2}{\varrho^2}c^2\right)^{\frac{1}{2}}\right\}.$$

The term under the integral sign is easily seen to be (as we know *à priori* it must be) a complete differential. It is convenient however to transform it thus. First, we have $\varrho d\varrho+zdz=rdr$; next, let the *latitude* of the body (or the angle between r and the plane of x, y) be λ; then $\tan\lambda=\frac{z}{\varrho}$, and

$$\varrho dz-zd\varrho=r^2d\lambda,\ \frac{r^2}{\varrho^2}=\sec^2\lambda.$$

Making these substitutions, the expression for V becomes

$$V=c\theta+\int\frac{dr}{r}(2mr^3(h+\varphi(r))-k^2)^{\frac{1}{2}}+\int d\lambda(k^2-c^2\sec^2\lambda)^{\frac{1}{2}}.$$

The integration in the second term cannot be effected till the form of the function $\varphi(r)$ is given: that of the third term may be more conveniently performed after the differentiations with respect to c and k, as in the next article.

29. The remaining integrals* of the problem are (art. 19.)

$$\frac{dV}{dk}=\alpha,\ \frac{dV}{dc}=\beta,\ \frac{dV}{dh}=t+\tau.$$

Performing the operations indicated, and observing that

$$\int\frac{d\lambda}{\sqrt{k^2-c^2\sec^2\lambda}}=\frac{1}{k}\sin^{-1}\left(\frac{k\sin\lambda}{\sqrt{k^2-c^2}}\right)$$

and

$$\int\frac{\sec^2\lambda d\lambda}{\sqrt{k^2-c^2\sec^2\lambda}}=\frac{1}{c}\sin^{-1}\left(\frac{c\tan\lambda}{\sqrt{k^2-c^2}}\right),$$

* It would perhaps be better to use the term "integral equations" here, in order to reserve the term "integral" for the case of an equation involving only one arbitrary constant (see art. 23.). The equations $\frac{dV}{dk}=\alpha$, &c. become "integrals" in this sense, when for k, c, and h, on the left, are substituted the functions of the variables to which they are respectively equal (from (i.), (ii.), (iii.)). An "integral" in this limited meaning is what is commonly called a "first integral," when the problem is considered as the solution of n differential equations of the second order. And any equation obtained by combining "integrals" so as to eliminate a set of n of the variables x_1, x_2, ... x_n, y_1, y_2, ... y_n, of which no two are conjugate, corresponds to what is commonly called a "final integral."

we obtain for the final integrals,

$$m\int r dr\{2mr^2(h+\varphi(r))-k^2\}^{-\frac{1}{2}}=t+\tau. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

$$\theta-\sin^{-1}\left(\frac{c\tan\lambda}{\sqrt{k^2-c^2}}\right)=\beta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

$$-k\int\frac{dr}{r}\left\{2mr^2(h+\varphi(r))-k^2\right\}^{-\frac{1}{2}}+\sin^{-1}\left(\frac{k\sin\lambda}{\sqrt{k^2-c^2}}\right)=\alpha. \quad . \quad \text{(vi.)}$$

Let $\frac{c}{k}=\cos\iota$; then $\frac{c}{\sqrt{k^2-c^2}}=\cot\iota$, and the equation (v.) becomes

$$\tan\lambda=\tan\iota.\sin(\theta-\beta), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v.a)}$$

which expresses that the orbit is in a plane whose inclination to the plane of x, y is ι. Also β is evidently the longitude of the node, reckoned from the axis of x.

The last term on the left of (vi.) becomes

$$\sin^{-1}\left(\frac{\sin\lambda}{\sin\iota}\right).$$

Now if ϑ be the "argument of latitude" or the angle between the node and the radius vector r, we have evidently $\sin\vartheta=\frac{\sin\lambda}{\sin\iota}$, so that the above term is simply ϑ, and the integral (vi.) becomes

$$\vartheta-\alpha=k\int\frac{dr}{r}\left\{2mr^2(h+\varphi(r))-k^2\right\}^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad \text{(vi.a)}$$

30. To apply the above expressions to the case of the undisturbed motion of a planet, we have only to put $\varphi(r)=\frac{\mu m}{r}$, where m is now the mass of the planet, and μ the sum of the masses of the sun and planet, the origin of coordinates being placed at the sun. It would be useless to give the well-known expressions to which the integrations now lead, my object being merely to obtain a set of *normal elements*. Now in this case we have (by well-known theorems), if a be the semiaxis major, e the excentricity, and ι as before the inclination,

$$h=\frac{-\mu}{2a}, \quad k=\sqrt{\mu a(1-e^2)},$$

and therefore $$c=\sqrt{\mu a(1-e^2)}.\cos\iota.$$

Also, if we take for the inferior limit of the integrations in (iv.) and (vi.a) the minimum value of r, or the perihelion distance, it is plain that α will be the longitude of the node, reckoned from the perihelion in the plane of the orbit, and $-\tau$ the time of perihelion passage. Thus we have the following six elements, arranged in conjugate pairs:—

$-\frac{\mu}{2a}$,	$-$(time of perihelion passage)
$\sqrt{\mu a(1-e^2)}$,	(angle between node and perihelion)
$\sqrt{\mu a(1-e^2)}.\cos\iota$,	(longitude of node).

It is obvious that we may change the signs of the first pair. And generally, that if f, g be any two conjugate elements, we may substitute for them λf, $\frac{1}{\lambda}g$, where λ is any *determinate* constant, i. e. not a function of the elements*.

The above elements coincide with those given by Jacobi. My object has been merely to illustrate a mode of obtaining them which seems capable of useful applications.

31. As a second example I shall apply the method to the case of the motion of a solid body about a fixed point.

Let the fixed point be taken for the origin, and the principal axes of the body through that point for the axes of x, y, z. Let ξ, η, ζ refer to the same origin and to axes fixed in space; a, b, c being the direction-cosines of the axis of x referred to the fixed axes of ξ, η, ζ, and a', b', c'; a'', b'', c'' being respectively the direction-cosines of the axes of y and z. Let θ be the inclination of the plane of x, y (or "equator") to that of ξ, η (or "ecliptic"); ψ the longitude of the node, reckoned from the axis of ξ, and φ the right-ascension of the axis of x. Then if A, B, C be the Moments of Inertia, and p, q, r the angular velocities, about the axes of x, y, z, the expression for the *vis viva* is $\mathrm{T}=\frac{1}{2}(\mathrm{A}p^2+\mathrm{B}q^2+\mathrm{C}r^2)$, where

$$p=-\theta'\cos\varphi-\psi'\sin\varphi\sin\theta$$
$$q=\theta'\sin\varphi-\psi'\cos\varphi\sin\theta$$
$$r=\varphi'+\psi'\cos\theta.$$

Let u, v, w be the variables conjugate respectively to θ, φ, ψ, so that

$$u=\frac{d\mathrm{T}}{d\theta'},\quad v=\frac{d\mathrm{T}}{d\varphi'},\quad w=\frac{d\mathrm{T}}{d\psi'},$$

the following expressions will be found without difficulty:

$$\mathrm{A}p=-u\cos\varphi+\frac{\sin\varphi}{\sin\theta}(v\cos\theta-w)$$

$$\mathrm{B}q=u\sin\varphi+\frac{\cos\varphi}{\sin\theta}(v\cos\theta-w)$$

$$\mathrm{C}r=v.$$

Considering at present only the case in which no forces act, we have the integral of *vis viva* $\mathrm{T}=h$, which becomes

$$\frac{1}{\mathrm{A}}\left(-u\cos\varphi+\frac{\sin\varphi}{\sin\theta}(v\cos\theta-w)\right)^2$$
$$+\frac{1}{\mathrm{B}}\left(u\sin\varphi+\frac{\cos\varphi}{\sin\theta}(v\cos\theta-w)\right)^2$$
$$+\frac{1}{\mathrm{C}}v^2=2h. \qquad \text{(i.)}$$

* More generally, we may substitute for f, g any two functions of them, p, q, such that

$$\frac{dp}{dg}\frac{dq}{df}-\frac{dp}{df}\frac{dq}{dg}=1,$$

a condition which requires the solution of a linear partial differential equation for the determination of one function, if the other be assumed. But on the subject of the transformation of elements see below, arts. 34, 35.

The three integrals which express the conservation of areas, namely,

$$Aap+Ba'q+Ca''r=e,$$
$$Abp+Bb'q+Cb''r=f,$$
$$Acp+Bc'q+Cc''r=g,$$

become, after simple reductions,

$$-u\cos\psi-\frac{\sin\psi}{\sin\theta}(v-w\cos\theta)=e$$
$$-u\sin\psi+\frac{\cos\psi}{\sin\theta}(v-w\cos\theta)=f$$
$$w=g.$$

Let $e^2+f^2+g^2=k^2$; we have, adding the squares of these three equations,

$$u^2+w^2+\frac{(v-w\cos\theta)^2}{\sin^2\theta}=k^2, \quad \ldots\ldots\ldots\ldots \text{(ii.)}$$

and we may take the three equations (i.), (ii.), and

$$w=g \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(iii.)}$$

as three normal integrals; the conditions

$$[g, h]=0, \quad [h, k]=0, \quad [k, g]=0$$

being obviously satisfied.

These three equations determine u, v, w as functions of θ, φ, ψ; and supposing the three former variables to be explicitly expressed in terms of the latter, we should have at once the three partial differential coefficients $\frac{dV}{d\theta}$, $\frac{dV}{d\varphi}$, $\frac{dV}{d\psi}$; the determination of V would therefore depend upon simple integration, and the remaining integrals would be given by means of the three equations

$$\frac{dV}{dh}=t+\tau, \quad \frac{dV}{dg}=c_1, \quad \frac{dV}{dk}=c_2,$$

τ, c_1, c_2 being new arbitrary constants.

In the general case, however, the algebraical solution of the equations (i.), (ii.), (iii.) is impracticable, since the elimination of v and w leads to an equation of the fourth degree in u; nor does it seem possible to evade the difficulty by choosing a different combination of integrals, since it may be shown that the necessary conditions cannot be satisfied unless two at least of the combinations chosen are of the second degree in u, v, w.

32. Mr. CAYLEY has given* a solution of this problem, which, though differing totally in form and method from the above, resembles it in arriving exactly at a corresponding point. For in Mr. CAYLEY's equations (27.), (28.), Φ and ∇ are to be expressed as functions of v; but this requires the algebraical solution of the system (18.) for p, q, r, and is therefore impracticable. (The two equations (i.), (ii.) of the

* Cambridge and Dublin Mathematical Journal, vol. i. p. 167.

last article are merely transformations of the two first of Mr. CAYLEY's (18.); and (iii.), though not identical with the third, is of the same degree; so that the algebraical difficulty is precisely the same in both methods.)

33. If we suppose A=B, the algebraical difficulty disappears, and the solution of the problem can be explicitly completed. But on account of the importance and interest of this case I shall make it the subject of a separate section, in which it will also be shown that the solution of the general case may be made to depend upon it, by means of the variation of elements. (See Section III.)

34. Suppose any complete normal solution of the system of differential equations (I.), art. 14, be known, i. e. a solution involving the $2n$ elements

$$a_1, a_2, \dots a_n, \quad b_1, b_2, \dots b_n$$

which satisfy the conditions (23.), art. 9; then an infinite number of other sets of normal elements can always be found.

For if we determine the $2n$ quantities $\alpha_1, \dots \alpha_n, \beta_1, \dots \beta_n$, as functions of a_1, &c., b_1, &c. by the $2n$ equations

$$\frac{dA}{da_i}=b_i, \quad \frac{dA}{d\alpha_i}=\beta_i,$$

where A is any arbitrary function of

$$a_1, a_2, \dots a_n, \alpha_1, \alpha_2, \dots \alpha_n,$$

it is obvious that the whole of the reasoning by which the formulæ (19.), art. 7, were established may be repeated, merely putting A in place of X, and α, β instead of x, y. And repeating in like manner the reasoning of art. 9, *mutatis mutandis*, it will follow that if f, g represent any two of the $2n$ quantities α_1, &c., β_1, &c., the expression

$$\Sigma_i \frac{d(f, g)}{d(b_i, a_i)}$$

will be equal to unity if f, g be a pair of the form α_j, β_j, and will vanish in every other case. But it was also shown ((25.) art. 9) that the above expression is equivalent to $-[f, g]$; it follows then that

$$[\alpha_j, \beta_j]=-1, \quad [\alpha_i, \alpha_j]=[\alpha_i, \beta_j]=[\beta_i, \beta_j]=0^*;$$

or, in other words, that $\alpha_1, \dots \alpha_n, \beta_1, \dots \beta_n$, are a new set of normal elements.

This method however can hardly be of much use in practice, because we cannot (at least without the solution of partial differential equations) determine what form

* I shall have occasion to refer afterwards to M. DESBOVES' Memoir in LIOUVILLE's Journal, vol. xiii., "Démonstration de deux théorèmes de M. JACOBI." But it may be observed here that the proposition in the text is not the same as that expressed by the same notation in the memoir alluded to, p. 400. For M. DESBOVES uses the symbols $[a_i, a_j]$ in a different sense. His theorem, in the notation of the present paper, is

$$\Sigma_i \frac{d(a_i, b_i)}{d(f, g)}=1, \text{ or } =0,$$

according as f, g are of the form α_j, β_j or not, which is easily established without the help of relations analogous

of the function A will cause any of the new elements to be *given* functions of the old. But the problems most likely to occur may be solved in another way, as follows.

35. Assuming for the set $\alpha_1, \alpha_2, \ldots \alpha_n$, given functions of the set $a_1, a_2, \ldots a_n$ *only*, it is required to find $\beta_1, \ldots \beta_n$.

(It will be observed that the conditions $[\alpha_i, \alpha_j]=0$ are necessarily satisfied in this case by virtue of (25.), art. 9, since α_1, &c. do not involve b_1, &c.)

It is plain, that if the principal function X had been found from the n integrals $a_1, a_2, \ldots a_n$ (as in art. 14.), it would be changed into that which would be found from the n integrals $\alpha_1, \alpha_2, \ldots \alpha_n$, merely by introducing the expressions for $a_1, \ldots a_n$ in terms of $\alpha_1, \ldots \alpha_n$; which expressions would be found by algebraical inversion of the assumed equations which give the latter set as functions of the former. Let $\overline{\mathrm{X}}$ represent the function X thus transformed; we have then

$$\beta_i=\frac{d\overline{\mathrm{X}}}{d\alpha_i}=\frac{d\mathrm{X}}{da_1}\frac{da_1}{d\alpha_i}+\frac{d\mathrm{X}}{da_2}\frac{da_2}{d\alpha_i}+\ldots$$

$$=b_1\frac{da_1}{d\alpha_i}+b_2\frac{da_2}{d\alpha_i}+\ldots+b_n\frac{da_n}{d\alpha_i}. \quad \ldots\ldots\ldots \quad (38.)$$

Thus β_i is determined as a function of the old elements, since $\frac{da_1}{d\alpha_i}$, &c. may be expressed in terms of the latter. In like manner we should have a set of inverse equations

$$b_i=\beta_1\frac{d\alpha_1}{da_i}+\beta_2\frac{d\alpha_2}{da_i}+\ldots+\beta_n\frac{d\alpha_n}{da_i}, \quad \ldots\ldots\ldots \quad (39.)$$

which may be used instead of (38.).

It is apparent that β_1, &c. will involve in general the elements a_1, &c. as well as b_1, &c.

Conversely, if we assumed for β_1, &c. given functions of the set $b_1, \ldots b_n$ alone, we

to (19.), but would not answer our present purpose. I regret to use symbols with a meaning different from that which custom has to some extent sanctioned; but there seemed to be only a choice of difficulties.

Mr. Spottiswoode has suggested to me the employment of the symbols (analogous to Mr. Sylvester's "umbral" notation)

$$\left[\begin{matrix} u, & v, & w, & \ldots. \\ \frac{d}{dx}, & \frac{d}{dy}, & \frac{d}{dz}, & \ldots. \end{matrix}\right], \qquad \left[\begin{matrix} x, & y, & z, & \ldots \\ d_1, & d_2, & d_3 & \ldots \end{matrix}\right]$$

instead of those which I have used, namely,

$$\frac{d(u, v, w, \ldots)}{d(x, y, z, \ldots)}, \qquad d(x, y, z, \ldots.).$$

If these were adopted, the two forms (p, q), $[p, q]$ might be used without confusion in their usual significations. See note to art. 9. But although the "umbral" forms are more suggestive of the properties which belong to the above expressions as *determinants*, the other forms bring more into view the analogies which connect them with the differential calculus; and therefore, for the purposes of this paper, I have preferred them. And it is perhaps better, for the present, that different notations should be *tried*, than that any attempt should be made to fix upon a definitive system for subjects so recent as those connected with the theory of determinants.

should have, for determining α_1, &c., either of the systems

$$\alpha_i=\Sigma_j\left(a_j\frac{db_j}{d\beta_i}\right),\quad a_i=\Sigma_j\left(\alpha_j\frac{d\beta_j}{db_i}\right).\quad\ldots\ldots\ldots\quad(40.)$$

We might obtain in this way an indefinite variety of sets of elements for the case of elliptic motion, beginning with those given at the end of art. 30. But it will be better to defer this illustration till after the discussion of the Method of the Variation of Elements, which will form the subject of a future Section.

36. It results, from the investigations of this and the preceding Sections, that if a set of n integrals $a_1, a_2, \ldots a_n$ be given, satisfying the $\frac{n(n-1)}{2}$ conditions $[a_i, a_j]=0$, the determination of n more integrals $b_1, \ldots b_n$, constituting, with the given ones, a complete normal set, is a *determinate problem*, admitting of a unique solution, and always reducible (setting aside algebraical difficulties) to quadratures.

But if, out of a complete normal set, n be given of which one or more pairs are *conjugate*, then the completion of the set is no longer a determinate problem, since the remaining n integrals, containing also one or more conjugate pairs, admit, to some extent, of arbitrary transpositions and combinations, as is evident from considerations similar to those employed in arts. 13 and 35. Hence we should expect *à priori* that the problem would require the solution of partial differential equations.

It appears, indeed, at first sight, that having any n of the elements *given* functions of the variables, the relations established in art. 9, with the others included in the formula (21.), art. 9, would furnish more than a sufficient number of equations to determine explicitly all the partial differential coefficients of the remaining elements in terms of the variables*, at least in the case in which the principle of *vis viva* subsists, and the given integrals do not contain t. But it is certain from the above considerations that this cannot be the case, and therefore that the equations furnished by those conditions cannot be all independent. I have not at present attempted to show this directly, though it would probably be easy to do so.

Note on art. 2, *Section* I.

The theorem established in this article may be more shortly demonstrated as follows:—

Since $$d\Sigma_i(x_iy_i)=\Sigma_i(x_idy_i)+\Sigma_i(y_idx_i)$$

* The conditions $[a_i, b_i]=1$, $[a_i, b_j]=0$, $[b, b_j]=0$, $[a_i, a_j]=0$ will give, as is easily seen, $\frac{n(n-1)}{2}+n^2$ equations; and the analogous conditions (21.), art. 9, in which the summation refers to the *numerators* of the differential coefficients, will give the same number, so that upon the whole we shall apparently have $3n^2-n$ equations, to determine the $2n^2$ partial coefficients required.

It is not difficult to make mistakes in this subject. I was for some time under the impression that the problem could be solved when *any* n independent integrals were given. Even the illustrious JACOBI himself appears to have been misled, at first sight, as to the consequences of POISSON's theorem (art. 22.). See the beginning of M. BERTRAND's Memoir mentioned above; I do not know the fact from any other source.

and $\Sigma_i(y_i dx_i) = d\mathrm{X}$ (by (5.)),

we have $\Sigma_i(x_i dy_i) = d(-\mathrm{X} + \Sigma_i(x_i y_i))$,

an equation which must become identical when x_1, x_2, &c. on each side are expressed in terms of y_1, y_2, &c. But the right side being then a complete differential of a function of y_1, y_2, &c., the left side must be so also; hence the conditions $\frac{dx_i}{dy_j} = \frac{dx_j}{dy_i}$ *must subsist*. The investigation of art. 2 shows that they *do subsist*, and is therefore perhaps to be preferred.

Section III.—*On the Equations of Rotatory Motion.*

37. In this supplementary section I propose further to exemplify the preceding theory by exhibiting the application of it to the problem of rotation in a more detailed form than was consistent with the plan of the former part of this essay. For this purpose it will first be desirable to anticipate the subject of a future section, so far as to give a concise deduction of the method of the variation of elements in its simplest form.

38. *Variation of Elements.*—Suppose a complete *normal solution* of the system of differential equations

$$x_i' = \frac{d\mathrm{Z}}{dy_i}, \quad y_i' + \frac{d\mathrm{Z}}{dx_i} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{I.})$$

has been obtained, so that we have $2n$ elements, divided into two conjugate sets

$$a_1, a_2, \ldots a_n; \; b_1, b_2, \ldots b_n$$

as in the former articles, so that

$$[a_i, b_i] = 1, \quad [a_i, a_j] = [b_i, b_j] = [a_i, b_j] = 0.$$

It is required to express the solution of the system

$$x_i' = \frac{d\mathrm{Z}}{dy_i} + \frac{d\Omega}{dy_i}, \quad y_i' + \frac{d\mathrm{Z}}{dx_i} + \frac{d\Omega}{dx_i} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{I.a})$$

in the same form by means of *variable elements*. The disturbing function Ω may be a function of all the variables x_1, &c., y_1, &c., and may also contain t explicitly.

In the undisturbed problem we have $a_i' = 0$, $b_i' = 0$; i. e. the equations

$$\frac{da_i}{dt} + [\mathrm{Z}, a_i] = 0, \quad \frac{db_i}{dt} + [\mathrm{Z}, b_i] = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{e.})$$

(see art. 22.) subsist identically when x_1, &c., y_1, &c. are expressed in terms of the elements and t.

In the disturbed problem, x_1, &c., y_1, &c. are to be the same functions of the elements and t as before; hence the equations (e.) continue to subsist identically, and therefore the values of a_i', b_i', namely,

$$a_i' = \frac{da_i}{dt} + [\mathrm{Z}, a_i] + [\Omega, a_i]$$

$$b_i' = \frac{db_i}{dt} + [\mathrm{Z}, b_i] + [\Omega, b_i],$$

become simply $a_i'=[\Omega, a_i]$, $b_i'=[\Omega, b_i]$.

In these expressions Ω, a_i, b_i are supposed to be expressed in terms of the variables. Now

$$[\Omega, a_i]=\Sigma_j \frac{d(\Omega, a_i)}{d(y_j, x_j)},$$

but, by equation (26.), art. 10, this is equivalent to

$$-\Sigma_j \frac{d(\Omega, a_i)}{d(b_j, a_j)},$$

in which Ω is expressed as a function of the elements and t; and this last expression obviously reduces itself to the single term $-\frac{d\Omega}{db_i}$. In like manner the expression for $[\Omega, b_i]$ reduces itself to $+\frac{d\Omega}{da_i}$; thus the equations for determining the variation of the elements are

$$a_i'=-\frac{d\Omega}{db_i}, \quad b_i'=\frac{d\Omega}{da_i}, \quad \ldots\ldots\ldots\ldots \text{(E.)}$$

in which Ω is to be expressed as a function of the elements and t*. This will be a sufficient account of the method for our immediate purpose.

39. The following propositions in spherical trigonometry will be required. If a, b, c be the sides, and α, β, γ the opposite angles of any spherical triangle, then

$$\cos(a+b)=\frac{\frac{(\cos\alpha+\cos\beta)^2}{1-\cos\gamma}-1-\cos\alpha\cos\beta}{\sin\alpha\sin\beta} \quad \ldots\ldots \text{(40.)}$$

$$\cos(a-b)=\frac{-\frac{(\cos\alpha-\cos\beta)^2}{1+\cos\gamma}+1-\cos\alpha\cos\beta}{\sin\alpha\sin\beta}; \quad \ldots\ldots \text{(41.)}$$

and if the sides be considered as functions of the angles, then

$$\frac{da}{d\beta}=\cos\gamma\frac{db}{d\beta}+\cos\beta\frac{dc}{d\beta} \quad \ldots\ldots\ldots \text{(42.)}$$

$$\frac{da}{d\gamma}=\cos\gamma\frac{db}{d\gamma}+\cos\beta\frac{dc}{d\gamma}. \quad \ldots\ldots\ldots \text{(43.)}$$

The two last are easily verified; but as the others are not so obvious, I shall give the demonstration. Putting x for the expression on the right of the equation (40.), we

* The history of these remarkable formulæ may, I believe, be stated as follows. They were first discovered by Lagrange in the case in which a_i, b_i were the *initial values* of x_i, y_i, and Ω contained x_1, &c. but not y_1, &c. They were extended by Sir W. R. Hamilton to the case in which Ω contains *both* sets of variables; and finally, by Jacobi, to the case in which a_1, &c., b_1, &c. are *any* system of conjugate elements. Jacobi however does not appear to have published a demonstration of them, and the only one which I have seen is by M. Desboves, Liouville's Journal, vol. xiii. p. 397, and differs essentially from that given in the text. Sir W. R. Hamilton has pointed out the circumstance, that when Ω contains both sets of variables, the varying elements determined by the formula (E.) are not *osculating*.

easily obtain

$$\frac{1-x}{1+x}=\frac{\cos^2\frac{\alpha-\beta}{2}\ \sin^2\frac{\gamma}{2}-\cos^2\frac{\alpha+\beta}{2}}{\cos^2\frac{\alpha+\beta}{2}\ \cos^2\frac{\alpha-\beta}{2}-\sin^2\frac{\gamma}{2}}$$

$$=-\frac{\cos^2\frac{\alpha-\beta}{2}\ \cos\frac{\alpha+\beta+\gamma}{2}\cos\frac{\alpha+\beta-\gamma}{2}}{\cos^2\frac{\alpha+\beta}{2}\ \cos\frac{\alpha-\beta+\gamma}{2}\cos\frac{\beta+\gamma-\alpha}{2}}$$

$$=\frac{\cos^2\frac{\alpha-\beta}{2}}{\cos^2\frac{\alpha+\beta}{2}}\tan^2\frac{c}{2}=\tan^2\frac{a+b}{2};$$

whence it is plain that $x=\cos(a+b)$, and in like manner may the equation (41.) be established.

40. Returning now to the problem of rotation, and supposing, for convenience, that the question refers to the motion of the earth about its centre of gravity, the following will be the signification of the symbols employed.

A, B, C are the moments of inertia about the principal axes of the earth, viz. the axes of x, y, z; the last being the polar axis, and the arrangement being such that the positive direction of z is to the *north* pole, and that the positive axis of x *follows* that of y in the actual rotation about the polar axis: p, q, r being the angular velocities about the three principal axes, the usual convention will be adopted as to their signs; so that in the actual case r is positive. The arrangement of the fixed axes of ξ, η, ζ is supposed similar to that of x, y, z, the plane of ξ, η being a fixed ecliptic, and the axis of ξ the origin of longitudes unless another origin be expressly indicated.

Then θ is the oliquity, ψ the longitude of the vernal equinox, and φ the right ascension of the axis of x; all referring to the fixed ecliptic.

Let the "principal plane" signify that which, in the undisturbed problem, is the "invariable plane." Then i is the inclination of the principal plane to the fixed ecliptic, and j is the inclination of the equator to the principal plane.

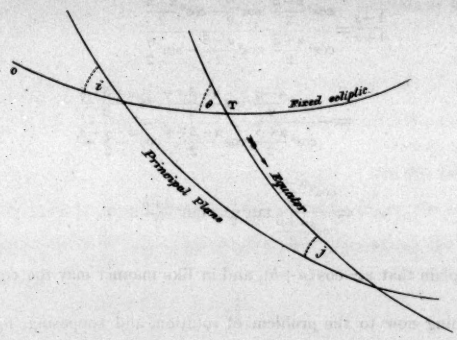
In the case of the earth, A is nearly equal to B, θ never differs sensibly from i, and j is therefore always small. But these conditions are not supposed in what follows. It is assumed however that C is the greatest of the three moments of inertia. These conventions, in which it is very desirable to avoid any ambiguity, may be illustrated by the annexed figure, in which O represents the origin of longitudes.

The angles of the spherical triangle formed by the intersection of the three planes with a spherical surface are $i, j, \pi-\theta$; and the sides opposite to them will be denoted by I, J, Θ. Thus we shall have

$$\cos \mathrm{I}=\frac{\cos i-\cos j\cos\theta}{\sin j\sin\theta},\quad \cos \mathrm{J}=\frac{\cos j-\cos i\cos\theta}{\sin i\sin\theta}$$

$$\cos\theta=\cos i\cos j-\sin i\sin j\cos\Theta.$$

And, in the figure, $O\Upsilon=\psi$, and φ is measured from Υ in the direction indicated by



the arrow, which is also the direction of the rotation about the polar axis. Moreover, if the direction-cosines of the axes of x, y, z referred to the fixed axes, be respectively a, b, c; a', b', c'; a'', b'', c'', we shall have

$$\begin{aligned}
a &= \cos\psi\cos\varphi - \sin\psi\sin\varphi\cos\theta \\
a' &= -\cos\psi\sin\varphi - \sin\psi\cos\varphi\cos\theta \\
a'' &= -\sin\psi\sin\theta \\
b &= \sin\psi\cos\varphi + \cos\psi\sin\varphi\cos\theta \\
b' &= -\sin\psi\sin\varphi + \cos\psi\cos\varphi\cos\theta \\
b'' &= \cos\psi\sin\theta \\
c &= -\sin\varphi\sin\theta \\
c' &= -\cos\varphi\sin\theta \\
c'' &= \cos\theta \\
p &= -\theta'\cos\varphi - \psi'\sin\varphi\sin\theta \\
q &= \theta'\sin\varphi - \psi'\cos\varphi\sin\theta \\
r &= \varphi' + \psi'\cos\theta,
\end{aligned}$$

hence we obtain the expressions for u, v, w employed in art. 31, viz.

$$u=\frac{dh}{d\theta}=-Ap\cos\varphi+Bq\sin\varphi$$

$$v=\frac{dh}{d\varphi}=Cr$$

$$w=\frac{dh}{d\psi}=-Ap\sin\varphi\sin\theta-Bq\cos\varphi\sin\theta+Cr\cos\theta,$$

from which the following also are easily deduced:

$$u=\frac{A+B}{2}\theta'+\frac{A-B}{2}(\theta'\cos 2\varphi+\psi'\sin\theta\sin 2\varphi)$$

$$v=C(\varphi'+\psi'\cos\theta)$$

$$w=\frac{A+B}{2}\psi'\sin^2\theta+C\cos\theta(\varphi'+\psi'\cos\theta)+\frac{A-B}{2}\sin\theta(\theta'\sin 2\varphi-\psi'\sin\theta\cos 2\varphi).$$

41. Resuming the three integrals (i.), (ii.), (iii.) of art. 31, we may put the first in the following form:—

$$Z+\Omega=h, \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(i.)}$$

in which
$$2Z=\frac{1}{2}\left(\frac{1}{A}+\frac{1}{B}\right)\left(u^2+\frac{(v\cos\theta-w)^2}{\sin^2\theta}\right)+\frac{v^2}{C}$$

$$2\Omega=\frac{1}{2}\left(\frac{1}{A}-\frac{1}{B}\right)\left\{\left(u^2-\frac{(v\cos\theta-w)^2}{\sin^2\theta}\right)\cos 2\varphi-\frac{2u(v\cos\theta-w)}{\sin\theta}\sin 2\varphi\right\};$$

and the other two are, as before,

$$w^2+u^2+\frac{(v-w\cos\theta)^2}{\sin^2\theta}=k^2 \quad \ldots\ldots\ldots\ldots \text{(ii.)}$$

$$w=g, \quad \ldots\ldots\ldots\ldots \text{(iii.)}$$

in which k is the sum of areas on the invariable plane, and g the sum on fixed ecliptic; moreover $v=Cr$ is the sum of areas projected on the plane of the equator; hence we have

$$g=k\cos i, \quad v=k\cos j.$$

It has been seen that the complete solution of the problem is impracticable in the general case, on account of an algebraical difficulty. If however we suppose B=A, this difficulty disappears; and after completing the solution on this supposition we may take account of the terms arising from the inequality of A and B, by treating the function denoted above by Ω (equation (i.)) as a *disturbing function*, and applying the method explained in art. 38. Thus when the action of disturbing forces is considered, the whole disturbing function will consist of two parts; one depending upon the forces, and the other the function which has just been assigned, and of which the effect, as will be seen, is extremely simple.

42. We proceed then first to complete the solution on the supposition A=B. The three integrals (i.), (ii.), (iii.) give in this case

$$v^2=\frac{C}{C-A}(k^2-2Ah), \quad w=g \quad \ldots\ldots\ldots\ldots \text{(44.)}$$

$$u=\frac{1}{\sin\theta}\left\{k^2-v^2-w^2+2vw\cos\theta-k^2\cos^2\theta\right\}^{\frac{1}{2}},$$

in which latter expression the above constant values of v and w are to be introduced. We may put, as before, $g=k\cos i$, $v=k\cos j$, j being now constant; and the expression for u becomes

$$u=\frac{k}{\sin\theta}\left\{1-\cos^2 i-\cos^2 j+2\cos i\cos j\cos\theta-\cos^2\theta\right\}^{\frac{1}{2}} \quad \ldots \text{(45.)}$$

and we shall have (art. 19.)

$$V=k(\psi\cos i+\varphi\cos j)+\int u d\theta; \quad \ldots\ldots\ldots\ldots \quad (46.)$$

and we will take

$$h,\ \cos i,\ \cos j$$

for *normal elements**, so that k is to be considered as a function of these elements, given by the equation (see (44.))

$$k^2=\frac{2ACh}{C-(C-A)\cos^2 j} \quad \ldots\ldots\ldots\ldots \quad (47.)$$

It is to be observed, that, according to the hypotheses admitted above, k is positive; also, the expression for u at the end of art. 40 becomes, in the case now considered, $u=A\theta'$. Thus u has the same sign as θ'; and since θ is evidently comprised between $i-j$ and $i+j$, if we suppose i and j both acute (as in the figure), $\sin\theta$ is always positive; hence in the expression (45.) for u, we have to attribute the sign + or − to the radical, *according as θ is increasing or diminishing*, or according as Θ is between 0 and π, or not; thus, in the position represented in the figure, the negative sign must be taken.

43. If we put $\pm Q$ for the radical in question, the expression for $ud\theta$ is easily transformed into the following, namely,

$$ud\theta=\pm\frac{k\sin\theta d\theta}{Q}\left\{1-\frac{1}{2}\frac{(\cos j-\cos i)^2}{1-\cos\theta}-\frac{1}{2}\frac{(\cos j+\cos i)^2}{1+\cos\theta}\right\},$$

in which it is evident that the part within brackets is *positive* upon the whole, but each of the two last terms is essentially *negative*. The integration is now easily performed, and the result is

$$\int u d\theta=\pm kP,$$

where the *sign* is that which belongs to the radical Q, and P is given by the equation

$$P=\cos^{-1}\frac{\cos\theta-\cos i\cos j}{\sin i\sin j}$$

$$-\frac{1}{2}(\cos j-\cos i)\cos^{-1}\frac{\dfrac{(\cos j-\cos i)^2}{1-\cos\theta}-1+\cos i\cos j}{\sin i\sin j}$$

$$+\frac{1}{2}(\cos j+\cos i)\cos^{-1}\frac{\dfrac{(\cos j+\cos i)^2}{1+\cos\theta}-1-\cos i\cos j}{\sin i\sin j},$$

+ an arbitrary function of i, j, h.

This apparently complicated expression has a very simple geometrical signification;

* Since g, h, k are normal elements (i. e. satisfy the conditions $[g, h]=0$, $[h, k]=0$, $[k, g]=0$, art. 31.), any three independent combinations of them are obviously normal also.

for, referring to the figure, and using the theorems (40.), we see that it is equivalent to

$$P = \cos^{-1}(-\cos\Theta) + \frac{\cos j + \cos i}{2}\cos^{-1}(\cos(I+J))$$

$$-\frac{\cos j - \cos i}{2}\cos^{-1}(-\cos(I-J)) + K,$$

where K is put for the arbitrary function. Now the expression for $u d\theta$ (from which this is derived) shows that the three terms in the above value of P must be so interpreted that the differential coefficient of the first (with respect to θ) shall be positive, and those of the two others negative. These conditions will be satisfied by taking*

$$\pm P = \pi - \Theta + \frac{\cos j + \cos i}{2}(I+J)$$

$$-\frac{\cos j - \cos i}{2}(\pi - (I-J)) + K$$

(in which the upper sign is to be taken when Θ is between 0 and π, and the under sign when Θ is $> \pi$).

Hence, assuming the arbitrary K so as to destroy the constant part of the expression, we have, without ambiguity, for all values of the variables,

$$\int u d\theta = k(\Theta - I\cos j - J\cos i),$$

so that, finally,

$$V = k\{(\downarrow - I)\cos j + (\varphi - J)\cos i + \Theta\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48.)$$

It will be observed that without attention to the proper interpretation of ambiguous symbols, a completely erroneous expression for V might have been obtained.

44. The final equations will be (art. 19.)

$$\frac{dV}{dh} = t + \tau, \quad \frac{dV}{d\cos i} = \alpha, \quad \frac{dV}{d\cos j} = \beta,$$

τ, α, β being three new arbitrary constants, namely, the elements conjugate respectively to h, $\cos i$, $\cos j$.

In performing the differentiations, it is to be remembered that I, J, Θ do not contain h; and that, by the equations (42.), (43.), art. 39, the terms arising from the differentiation of I, J, Θ with respect to i and j, disappear identically, so that these functions may be considered as exempt from differentiation. Also we have

$$\frac{dk}{dh} = \frac{k}{2h}, \quad \frac{dk}{d\cos i} = 0,$$

$$\frac{dk}{d\cos j} = \frac{(C-A)k^3\cos j}{2ACh}$$

* In the figure, as θ diminishes (i and j remaining constant) Θ increases, $I+J$ increases, and $I-J$ increases or diminishes according as $j \lessgtr i$, since $\tan\frac{I-J}{2} = \tan\frac{\Theta}{2}\cdot\frac{\sin\frac{i-j}{2}}{\sin\frac{j+i}{2}}$.

(see equation (47.)), and the final equations become, after simple reductions,

$$\left.\begin{aligned} \Theta &= -\frac{\alpha\cos i+\beta\cos j}{k}+\frac{k}{\mathrm{A}}(t+\tau) \\ \varphi-\mathrm{I} &= \frac{\beta}{k}-\left(\frac{1}{\mathrm{A}}-\frac{1}{\mathrm{C}}\right)k\cos j.(t+\tau) \\ \psi-\mathrm{J} &= \frac{\alpha}{k} \end{aligned}\right\} \quad \ldots\ldots\ldots \text{(R.)}$$

These equations comprise a *normal solution* of the problem. The first gives immediately

$$\cos\theta = \cos i\cos j - \sin i\sin j\cos\left(\frac{k}{\mathrm{A}}(t+\tau)-\frac{\alpha\cos i+\beta\cos j}{k}\right)$$

(see art. 40.); and since I, J are given explicit functions of θ, the three variables θ, φ, ψ are determined explicitly as functions of t. The third equation (R.) simply expresses that the invariable plane intersects the ecliptic in a fixed line, whose longitude is $\frac{\alpha}{k}$.

45. Let us now introduce the supposition that A and B are unequal, and that the body is acted on by disturbing forces.

We must (see art. 41.) put $\frac{1}{2}\left(\frac{1}{\mathrm{A}}+\frac{1}{\mathrm{B}}\right)$ instead of $\frac{1}{\mathrm{A}}$ in the equations (R.) of the last article; these equations will express the solution of the problem, the elements being now variable, and determined as functions of t by the system of equations

$$h' = -\frac{d\Phi}{d\tau},\quad (\cos i)' = -\frac{d\Phi}{d\alpha},\quad (\cos j)' = -\frac{d\Phi}{d\beta}$$

$$\tau' = \frac{d\Phi}{dh},\quad \alpha' = \frac{d\Phi}{d\cos i},\quad \beta' = \frac{d\Phi}{d\cos j},$$

where Φ is the disturbing function, expressed in terms of the elements and t.

46. If there are no disturbing forces, Φ reduces itself simply to Ω (art. 41.), which is now to be transformed by means of the equations (R.), art. 44, as follows.

Since $v = k\cos j$, and $w = k\cos i$, we have

$$\frac{v\cos\theta - w}{\sin\theta} = -k\frac{\cos i-\cos j\cos\theta}{\sin\theta} = -k\sin j\cos \mathrm{I}.$$

Also the expression for u, art. 42, is easily put in the following form:

$$u = \frac{k}{\sin\theta}\left\{\sin^2 i\sin^2 j-(\cos\theta-\cos i\cos j)^2\right\}^{\frac{1}{2}}$$

$$= -\frac{k}{\sin\theta}\sin i\sin j\sin\Theta$$

(with respect to the sign, see art. 42.). And since

$$\frac{\sin\Theta}{\sin\theta} = \frac{\sin \mathrm{I}}{\sin i},$$

this becomes

$$u = -k\sin j\sin \mathrm{I}.$$

Introducing these expressions in the value of Ω (art. 41.), we find

$$\Omega = -\frac{k^2}{4}\left(\frac{1}{A}-\frac{1}{B}\right)\sin^2 j \cos 2(\varphi - I); \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49.)$$

and when $\varphi - I$ is expressed in terms of the elements and t (see equations (R.), art. 44, in which $\frac{1}{2}\left(\frac{1}{A}+\frac{1}{B}\right)$ is now to be written for $\frac{1}{A}$), this becomes, finally,

$$\Omega = -\frac{k^2}{4}\left(\frac{1}{A}-\frac{1}{B}\right)\sin^2 j . \cos 2\left[\frac{\beta}{k} - \left(\frac{1}{2}\left(\frac{1}{A}+\frac{1}{B}\right)-\frac{1}{C}\right)k \cos j . (t+\tau)\right]. \quad . \quad . \quad (\Omega.)$$

47. The above expression for Ω does not contain the elements i, α; hence, when there are no disturbing forces, we shall have $(\cos i)' = 0$, $\alpha' = 0$, or i and α are constant; also

$$k' = -\frac{dk}{dh}\frac{d\Omega}{d\tau} - \frac{dk}{d\cos j}\frac{d\Omega}{d\beta},$$

an expression which is easily found to vanish identically (see the values of $\frac{dk}{dh}$, $\frac{dk}{d\cos j}$ in art. 44, observing to put $\frac{1}{2}\left(\frac{1}{A}+\frac{1}{B}\right)$ for $\frac{1}{A}$). Thus k is also constant; and the "principal plane" is still the "invariable plane," as we know *à priori*.

48. If we now suppose the attraction of another body to be introduced as a disturbing force, we shall have to take for the disturbing function

$$\Phi = \Omega - P,$$

where Ω is the same as above, and P is the potential of one body upon the other, expressed as a function of the elements and the time*. And it follows from the remarks of the last article, that the variation in the *position of the principal plane* depends wholly upon P, and not upon Ω.

I shall here conclude this part of the subject, as it would be beyond the scope of this essay to enter into the details of any of the various problems which might be taken in illustration of the theory, such as those which relate to precession and nutation, or to the motion of the moon about its centre of gravity. The investigations of this section have been introduced, because the results, so far as they go, appeared interesting in themselves, and afforded a remarkable example of the application of the general method.

P.S. Since the last sheets of this essay were in type, I have seen for the first time two papers by Professor Brioschi, in Tortolini's Annali for August and October 1853, of which the titles are "Sulla variazione delle costanti arbitrarie nei problemi della Dinamica," and "Intorno ad un teorema de Meccanica." I have not had an opportunity of examining them sufficiently to judge how far any of the preceding investigations may have been anticipated in them.

June 7.

* The variables which determine the position of the disturbing body are supposed to be given explicit functions of t.

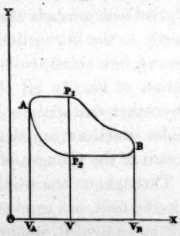
VI. *On the Geometrical Representation of the Expansive Action of Heat, and the Theory of Thermo-dynamic Engines.* *By* WILLIAM JOHN MACQUORN RANKINE, *C.E., F.R.SS. Lond. and Edin. &c.*

Received December 5, 1853,—Read January 19, 1854.

SECTION I.—INTRODUCTION AND GENERAL THEOREMS.

(Article 1.) THE first application of a geometrical diagram to represent the expansive action of Heat was made by JAMES WATT, when he contrived the well-known Steam-Engine Indicator, subsequently altered and improved by others in various ways. As the diagram described by WATT's Indicator is the type of all diagrams representing the expansive action of heat, its general nature is exhibited in fig. 1.

Fig. 1.



Let abscissæ, measured along, or parallel to, the axis OX represent the volumes successively assumed by a given mass of an elastic substance, by whose alternate expansion and contraction heat is made to produce motive power; OV_A and OV_B being the least and greatest volumes which the substance is made to assume, and OV any intermediate volume. For brevity's sake, these quantities will be denoted by V_A, V_B, and V, respectively. Then $V_B - V_A$ may represent the space traversed by the piston of an engine during a single stroke.

Let ordinates, measured parallel to the axis OY and at right angles to OX, denote the expansive pressures successively exerted by the substance at the volumes denoted by the abscissæ. During the increase of volume from V_A to V_B, the pressure, in order that motive power may be produced, must be, on the whole, greater than during the diminution of volume from V_B to V_A; so that, for instance, the ordinates VP_1 and VP_2, or the symbols P_1 and P_2, may represent the pressures corresponding to a given volume V during the expansion and contraction of the substance respectively.

Then the area of the curvilinear figure, or *Indicator-diagram*, AP_1BP_2A, will represent the motive power, or "Potential Energy," *developed* or *given out* during a complete stroke, or cycle of changes of volume of the elastic substance. The algebraical expression for this area is

$$\int_{V_A}^{V_B} (P_1 - P_2) dV. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.)$$

The practical use of such diagrams, in ascertaining the power and the mode of action of the steam in steam-engines, where the curve AP_1BP_2A is described by a pencil attached to a pressure-gauge, on a card whose motion corresponds with that of the piston, is sufficiently well known.

(2.) It appears that the earliest application of *diagrams of energy* (as they may be called) to prove and illustrate the theoretical principles of the mechanical action of heat, was made either by CARNÔT, or by M. CLAPEYRON in his account of CARNÔT's theory; but the conclusions of those authors were in a great measure vitiated by the assumption of the substantiality of heat.

In the fifth section of a paper on the Mechanical Action of Heat, published in the Transactions of the Royal Society of Edinburgh, vol. XX., a diagram of energy is employed to demonstrate the general law of the economy of heat in thermo-dynamic engines according to the correct principle of the action of such machines, viz. that the area of the diagram represents at once the potential energy or motive power which is developed at each stroke, and the mechanical equivalent of the actual energy, or heat, which permanently disappears.

As the principles of the expansive action of heat are capable of being presented to the mind more clearly by the aid of diagrams of energy than by means of words and algebraical symbols alone, I purpose, in the present paper, to apply those diagrams, partly to the illustration and demonstration of propositions already proved by other means, but chiefly to the solution of new questions, especially those relating to the action of heat in all classes of engines, whether worked by air, or by steam, or by any other material; so as to present, in a systematic form, those theoretical principles which are applicable to all methods of transforming heat to motive power by means of the changes of volume of an elastic substance.

Throughout the whole of this investigation, quantities of heat, and coefficients of specific heat, are expressed, not by units of temperature in a unit of weight of water, but by equivalent quantities of mechanical power, stated in foot-pounds, according to the ratio established by Mr. JOULE's experiments on friction (Phil. Trans. 1850); that is to say,

772 foot-pounds per degree of FAHR., or
1389·6 foot-pounds per Centigrade degree,

applied to one pound of liquid water at atmospheric temperatures.

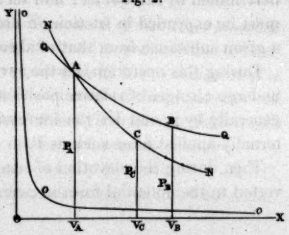
(3.) *Of Isothermal Curves, and Curves of No Transmission of Heat.*

A curve described on a diagram of energy, such that its ordinates represent the pressures of a homogeneous substance corresponding to various volumes, while the total *sensible* or *actual heat* present in the body is maintained at a constant value, denoted, for example, by Q, may be called the *Isothermal Curve of Q* for the given substance. (See fig. 2.) Suppose, for instance, that the co-ordinates of the point A, V_A and P_A, represent respectively a volume and a pressure of a given substance, at which the actual heat is Q; and the co-ordinates of the point B, viz. V_B and P_B, another

volume and pressure at which the actual heat is the same; then are the points A and B situated on the same isothermal curve QQ.

On the other hand, let the substance be allowed to expand from the volume and pressure V_A, P_A, without receiving or emitting heat; and when it reaches a certain volume, V_C, let the pressure be represented by P_C, which is less than the pressure would have been had the actual heat been maintained constant, because, by expansion, heat is made to disappear. Then C will be a point on a certain curve NN passing through A, which may be called a *Curve of No Transmission*.

Fig. 2.



It is to be understood that, during the process last described, the potential energy developed during the expansion, and which is represented by the area ACV_CV_A, is entirely communicated to external substances; for if any part of it were expended in agitating the particles of the expanding substance, a portion of heat would be reproduced by friction.

If *o o o* be a curve whose ordinates represent the pressures corresponding to various volumes when the substance is absoletely destitute of heat, then this curve, which may be called the *Curve of Absolute Cold*, is at once an isothermal curve and a curve of no transmission.

So far as we yet know, the curve of absolute cold is, for all substances, an asymptote to all the other isothermal curves and curves of no transmission, which approach it and each other indefinitely as the volume of the substance increases without limit.

NOTE.—The following remarks are intended to render more clear the precise meaning of the term *Total Actual Heat*.

The Total Actual Heat of a given mass of a given substance at a given temperature, is the quantity of Physical Energy present in the mass *in the form of Heat* under the given circumstances.

If, for the purpose of illustrating this definition, we assume the hypothesis that heat consists in molecular revolutions of a particular kind, then the Total Actual Heat of a mass is measured by the mechanical power corresponding to the *vis viva* of those revolutions, and is represented by

$$\frac{1}{2}\Sigma.mv^2,$$

m being the mass of any circulating molecule, and v^2 the mean-square of its velocity.

But the meaning of the term Total Actual Heat may also be illustrated without the aid of any hypothesis.

For this purpose, let us take the ascertained fact of the production of heat by the expenditure of mechanical power in friction, according to the numerical proportion determined by Mr. JOULE; and let E denote the quantity of mechanical power which must be expended in friction, in order to raise the temperature of unity of weight of a given substance from that of absolute privation of heat to a given temperature τ.

During this operation, let the several elements of the external surface of the mass undergo changes of relative position expressed by the variations of quantities denoted generally by p, and let the increase of each such quantity as p be resisted by an externally-applied force such as P.

Then during the elevation of temperature from absolute cold to τ, the energy converted to the potential form in overcoming the external pressures P will be

$$\Sigma.\int \mathrm{P}dp.$$

Also let the internal particles of the mass undergo changes of relative position expressed by the variations of quantities denoted generally by r, and let the increase of each such quantity as r be resisted by an internal molecular force such as R.

Then the energy converted to the potential form in overcoming internal molecular forces will be

$$\Sigma.\int \mathrm{R}dr.$$

Subtracting these quantities of energy converted to the potential form by means of external pressures and internal forces, from the whole power converted into heat by friction in order to raise the temperature of the mass from that of absolute privation of heat to the given temperature τ, we find the following result:—

$$\mathrm{Q}=\mathrm{E}-\Sigma.\int \mathrm{P}dp-\Sigma.\int \mathrm{R}dr;$$

and this remainder is the quantity of energy which *retains the form of heat*, in unity of weight of the given substance at the given temperature; that is to say, the Total Actual Heat.

It is obvious that Total Actual Heat cannot be ascertained directly; first, because the temperature of total privation of heat is unattainable; and secondly, because the molecular forces R are unknown.

It can, however, be determined indirectly from the latent heat of expansion of the substance. For the heat which disappears during the expansion of unity of weight of an elastic substance at constant actual heat from the volume $\mathrm{V_A}$ to the volume $\mathrm{V_B}$, under the constant or variable pressure P, is expressed (as will be shown in the sequel) by

$$\mathrm{Q}.\frac{d}{d\mathrm{Q}}\int_{\mathrm{V_A}}^{\mathrm{V_B}} \mathrm{P}d\mathrm{V};$$

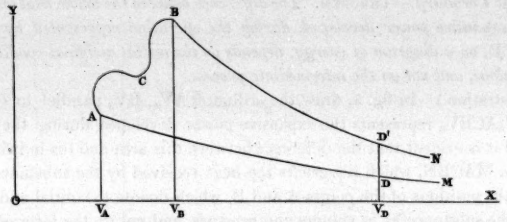
so that from a sufficient number of experiments on the amount of heat transformed

to potential energy by the expansion of a given substance, the relations, for that substance, between pressure, volume, and Total Actual Heat, may be determined.

(4.) PROPOSITION I.—THEOREM. *The Mechanical Equivalent of the Heat absorbed or given out by a substance in passing from one given state as to pressure and volume to another given state, through a series of states represented by the co-ordinates of a given curve on a diagram of energy, is represented by the area included between the given curve and two curves of no transmission of heat drawn from its extremities, and indefinitely prolonged in the direction representing increase of volume.*

(Demonstration) (see fig. 3). Let the co-ordinates of any two points, A and B, represent respectively the volumes and pressures of the substance in any two condi-

Fig. 3.



tions; and let a curve of any figure, ACB, represent, by the co-ordinates of its points, an arbitrary succession of volumes and pressures through which the substance is made to pass, in changing from the condition A to the condition B. From the points A and B respectively, let two curves of no transmission AM, BN, extend indefinitely towards X; then the area referred to in the enunciation is that contained between the given arbitrary curve ACB and the two indefinitely prolonged curves of no transmission; areas above the curve AM being considered as representing heat absorbed by the substance, and those below, heat given out.

To fix the ideas, let us in the first place suppose the area MACBN to be situated above AM. After the substance has reached the state B, let it be expanded according to the curve of no transmission BN, until its volume and pressure are represented by the co-ordinates of the point D'. Next, let the volume V_D be maintained constant, while heat is abstracted until the pressure falls so as to be represented by the ordinate of the point D, situated on the curve of no transmission AM. Finally, let the substance be compressed, according to this curve of no transmission, until it recovers its primitive condition A. Then the area ACBD'DA, which represents the whole potential energy developed by the substance during one cycle of operations, represents also the heat which disappears, that is, the difference between the heat absorbed by the substance during the change from A to B, and emitted during the

change from D′ to D; for if this were not so, the cycle of operations would alter the amount of energy in the universe, which is impossible.

The further the ordinate $V_D DD'$ is removed in the direction of X, the smaller does the heat emitted during the change from D′ to D become; and consequently, the more nearly does the area ACBD′DA approximate to the equivalent of the heat absorbed during the change from A to B; to which, therefore, the area of the indefinitely-prolonged diagram MACBN is exactly equal. Q.E.D.

It is easy to see how a similar demonstration could have been applied, *mutatis mutandis*, had the area lain below the curve AM. It is evident also, that when this area lies, part above and part below the line AM, the difference between these two parts represents the difference betweeu the heat absorbed and the heat emitted during different parts of the operation.

(5.) *First Corollary.*—THEOREM. *The difference between the whole heat absorbed, and the whole expansive power developed, during the operation represented by any curve, such as* ACB, *on a diagram of energy, depends on the initial and final conditions of the substance alone, and not on the intermediate process.*

(Demonstration.) In fig. 3, draw the ordinates AV_A, BV_B parallel to OY. Then the area $V_A ACBV_B$ represents the expansive power developed during the operation ACB; and it is evident that the difference between this area and the indefinitely-prolonged area MACBN, which represents the heat received by the substance, depends simply on the positions of the points A and B, which denote the initial and final conditions of the substance as to volume and pressure, and not on the form of the curve ACB, which represents the intermediate process. Q.E.D.

To express this result symbolically, it is to be considered, that the excess of the heat or actual energy *received* by the substance above the expansive power or potential energy *given out* and exerted on external bodies, in passing from the condition A to the condition B, is equal to the whole energy *stored up* in the substance during this operation, which consists of two parts, viz.—

Actual energy; being the increase of the actual or sensible heat of the substance in passing from the condition A to the condition B, which is to be represented by this expression,

$$\Delta.Q = Q_B - Q_A;$$

Potential energy; being the power which is stored up in producing changes of molecular arrangement during this process; and which, it appears from the Theorem just proved, must be represented, like the actual energy, by the difference between a function of the volume and pressure corresponding to A, and the analogous function of the volume and pressure corresponding to B; that is to say, by an expression of the form,

$$\Delta S = S_B - S_A.$$

Let $H_{A,B}$ = area MACBN

represent the heat received by the substance during the operation ACB, and

$$\int_{V_A}^{V_B} P dV = \text{area } V_A A C B V_B$$

the power or potential energy, given out.

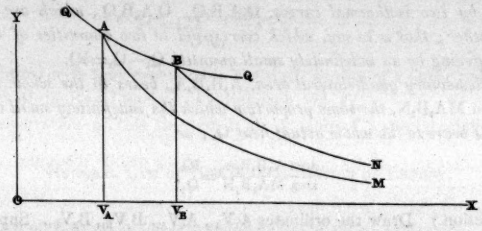
Then the theorem of this article is expressed as follows:—

$$H_{A,B} - \int_{V_A}^{V_B} P dV = Q_B - Q_A + S_B - S_A = \Delta Q + \Delta . S \quad . \quad . \quad . \quad . \quad (2.)$$

being a form of the General Equation of the Expansive Action of Heat, in which the *Potential of Molecular Action*, S, remains to be determined.

(6.) *Second Corollary* (see fig. 4).—The *Latent Heat of Expansion* of a substance, from one given volume V_A to another V_B, for a given amount of actual heat Q; that

Fig. 4.



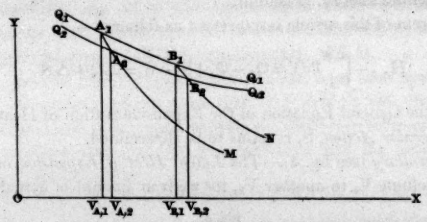
is to say, the heat which must be absorbed by the substance in expanding from the volume V_A to the volume V_B, in order that the actual heat Q may be maintained constant, is represented geometrically as follows. Let QQ be the isothermal curve of the given actual heat Q on the diagram of energy; A, B two points on this curve, whose co-ordinates represent the two given volumes and the corresponding pressures. Through A and B draw the two curves of no transmission AM, BN, produced indefinitely in the direction of X. Then the area contained between the portion of isothermal curve AB, and the indefinitely-produced curves AM, BN, represents the mechanical equivalent of the latent heat sought, whose symbolical expression is formed from Equation 2 by making $Q_B - Q_A = 0$, and is as follows:—

$$H_{A,B} \text{ (for Q=const.)} = \int_{V_A}^{V_B} P dV + S_B - S_A . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

SECTION II.—PROPOSITIONS RELATIVE TO HOMOGENEOUS SUBSTANCES.

(7.) PROPOSITION II.—THEOREM. *In fig.* 5, *let* A_1A_2M, B_1B_2N *be any two curves of no transmission, indefinitely extended in the direction of* X, *intersected in the points,*

Fig. 5.



A_1, B_1, A_2, B_2, *by two isothermal curves,* $Q_1A_1B_1Q_1$, $Q_2A_2B_2Q_2$, *which are indefinitely near to each other; that is to say, which correspond to two quantities of actual heat,* Q_1 *and* Q_2, *differing by an indefinitely small quantity* $Q_1 - Q_2 = \delta Q$.

Then the elementary quadrilateral area, $A_1B_1B_2A_2$, *bears to the whole indefinitely-prolonged area* MA_1B_1N, *the same proportion which the indefinitely small difference of actual heat* δQ *bears to the whole actual heat* Q_1; *or*

$$\frac{\text{area } A_1B_1B_2A_2}{\text{area } MA_1B_1N} = \frac{\delta Q}{Q_1}.$$

(Demonstration.) Draw the ordinates A_1V_{A1}, A_2V_{A2}, B_1V_{B1}, B_2V_{B2}. Suppose, in the first place, that δQ is an aliquot part of Q_1, obtained by dividing the latter quantity by a very large integer n, which we are at liberty to increase without limit.

The entire indefinitely-prolonged area MA_1B_1N represents a quantity of heat which is converted into potential energy during the expansion of the substance from V_{A1} to V_{B1}, in consequence of the continued presence of the total actual heat Q_1; for if no heat were present no such conversion would take place. *Mutatis mutandis*, a similar statement may be made respecting the area MA_2B_2N. By increasing without limit the number n and diminishing δQ, we may make the expansion from V_{A2} to V_{B2} as nearly as we please an identical phenomenon with the expansion from V_{A1} to V_{B1}. The quadrilateral $A_1B_1B_2A_2$ represents the diminution of conversion of heat to potential energy, which results from the abstraction of any one whatsoever of the n small equal parts δQ into which the actual heat Q_1 is supposed to be divided, and it therefore represents the effect, in conversion of heat to potential energy, of the presence of any one of those small portions of actual heat. And as all those portions δQ are similar and similarly circumstanced, the effect of the presence of the whole actual heat Q_1 in causing conversion of heat to potential energy, will be simply the sum of the effects of all its small portions, and will bear the same ratio to the effect of one of those small portions, which the whole actual heat bears to the small portion. Thus, by

virtue of the general law enunciated below and assumed as an axiom, the theorem is proved when δQ is an aliquot part of Q_1; but δQ is either an aliquot part, or a sum of aliquot parts, or may be indefinitely approximated to by a series of aliquot parts; so that the theorem is universally true. Q.E.D.

The symbolical expression of this theorem is as follows. When the actual heat Q_1, at any given volume, is varied by the indefinitely small quantity δQ, let the pressure vary by the indefinitely small quantity $\frac{dP}{dQ}\delta Q$; then the area of the quadrilateral $A_1B_1B_2A_2$ will be represented by

$$\delta Q . \int_{V_{A,1}}^{V_{B,1}} \frac{dP}{dQ} dV,$$

and consequently, that of the whole figure MA_1B_1N, or the latent heat of expansion from $V_{A,1}$ to $V_{B,1}$, at Q_1, by

$$H_1 = Q_1 \int_{V_{A1}}^{V_{B1}} \frac{dP}{dQ} dV ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

a result identical with that expressed in the sixth section of a paper published in the Transactions of the Royal Society of Edinburgh, vol. xx.

The demonstration of this theorem is an example of a special application of the following

General Law of the Transformation of Energy.

The effect of the presence, in a substance, of a quantity of Actual Energy, in causing transformation of Energy, is the sum of the effects of all its parts:—
a law first enunciated in a paper read by me to the Philosophical Society of Glasgow on the 5th of January, 1853.

(8.) General Equation of the Expansive Action of Heat.

The two expressions for the Latent Heat of Expansion at constant Actual Heat, given in equations 3 and 4 respectively, being equated, furnish the means of determining the potential energy of molecular action S, so far as it depends on volume, and thus of giving a definite form to the general equation 2.

The two expressions referred to may be thus stated in words:—

I. The heat which disappears in producing a given expansion, while the actual heat present in the substance is maintained constant, is equivalent to the sum of the potential energy given out in the form of expansive power, and the potential energy stored up by means of molecular attractions.

II. It is also equivalent to the potential energy due to the action during the expansion, of a pressure $Q\frac{dP}{dQ}$, at each instant equal to what the pressure would be, if its actual rate of variation with heat at the instant in question were a constant coefficient, expressing the ratio of the whole pressure to the whole actual heat present.

The combination of these principles, expressed symbolically, gives the following result :—

$$H_{A,B}(\text{for } Q=\text{const.})=Q\int_{V_A}^{V_B}\frac{dP}{dQ}dV=\int_{V_A}^{V_B}PdV+S_B-S_A;$$

whence we deduce the following general value for the potential of molecular action :—

$$S=\int\left(Q\frac{dP}{dQ}-P\right)dV+\varphi.Q, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.)$$

in which $\varphi.Q$ denotes some function of the total actual heat not depending on the density of the substance. This value being introduced into equation (2.), produces the following :—

$$H_{A,B}-\int_{V_A}^{V_B}PdV=Q_B-Q_A+S_B-S_A$$

$$=Q_B-Q_A+\varphi.Q_B-\varphi.Q_A+\int_{V_A}^{V_B}\left(Q\frac{dP}{dQ}-P\right)dV=\Psi_B-\Psi_A. \quad (6.)$$

The symbol $\Psi=Q+S$ is used to denote the sum of the actual energy of heat, and the potential energy of molecular action, present in the substance in any given condition.

The above is the General Equation of the Expansive Action of Heat in a homogeneous substance, and is the symbolical expression of the Geometrical Theorems I. and II. combined.

When the variations of actual heat and of volume become indefinitely small, this equation takes the following differential form :—

$$\left.\begin{aligned} d.\Psi=d.H-PdV=dQ+d.S=\left(1+\varphi'.Q+Q\frac{d^2}{dQ^2}\int PdV\right)dQ+\left(Q\frac{dP}{dQ}-P\right)dV \\ \text{otherwise} \qquad d.H=\frac{K_V}{k}.dQ+Q\frac{dP}{dQ}.dV \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned}\right\} \quad (7.)$$

The coefficient of dQ in the above expressions, viz.

$$\frac{K_V}{k}=1+\varphi'.Q+Q\frac{d^2}{dQ^2}\int PdV, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.)$$

is the ratio of the apparent specific heat of the substance at constant volume to its real specific heat; that is, the ratio of the whole heat consumed in producing an indefinitely small increase of actual heat, to the increase of actual heat produced.

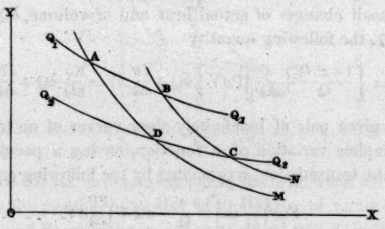
These general equations are here deduced independently of any special molecular hypothesis, as they also have been, by a method somewhat different, in the sixth section of a paper previously referred to*. Equations equivalent to the above have also been deduced from the Hypothesis of Molecular Vortices, in the paper already mentioned, and in a paper on the Centrifugal Theory of Elasticity in the same volume.

* Trans. Roy. Soc. Edinb. vol. xx.

(9.) *First Corollary from Proposition* II.—THEOREM. *If a succession of isothermal curves corresponding to quantities of heat diminishing by equal small differences* δQ, *be drawn across any pair of curves of no transmission, they will cut off a series of equal small quadrilaterals.*

Second Corollary.—THEOREM. *In fig.* 6, *let* ADM, BCN *be any two curves of no transmission, indefinitely prolonged in the direction of* X, *and let any two isothermal*

Fig. 6.



curves Q_1Q_1, Q_2Q_2, *corresponding respectively to any two quantities of actual heat* Q_1, Q_2, *be drawn across them. Then will the indefinitely-prolonged areas* MABN, MDCN, *bear to each other the simple ratio of the quantities of actual heat* Q_1, Q_2.

Or, denoting those areas respectively by H_1, H_2—

$$\frac{H_2}{H_1}=\frac{Q_2}{Q_1}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9.)$$

This corollary is the geometrical expression of the law of the maximum efficiency of a perfect thermo-dynamic engine, already investigated by other methods. In fact, the area MABN represents the whole heat expended, or the latent heat of expansion, the actual heat at which heat is received being Q_1; MDCN, the heat lost, or the latent heat of compression, which is carried off by conduction at the actual heat Q_2; and ABCD (being the indicator-diagram of such an engine), the motive power, produced by the permanent disappearance of an equivalent quantity of heat; and the *efficiency* of the engine is expressed by the ratio of the heat converted into motive power to the whole heat expended, viz.—

$$\frac{ABCD}{MABN}=\frac{H_1-H_2}{H_1}=\frac{Q_1-Q_2}{Q_1}. \quad \ldots\ldots\ldots\ldots (10.)$$

(10.) *Third Corollary* (*of Thermo-Dynamic Functions*).

If the two curves of no transmission in fig. 6, ADM, BCN, be indefinitely close together, the ratio of the heat consumed in passing from one of those curves to the other, to the actual heat present, will be the same, whatever may be the form and position of the curve indicating the mode of variation of pressure and volume, provided it intersects the two curves of no transmission at a finite angle; because the area contained between this connecting curve and the two indefinitely-prolonged curves

of no transmission will differ from an area whose upper boundary is an isothermal curve, by an indefinitely small area of the second order.

To express this symbolically, let

$$\frac{\delta H}{Q}=\delta F$$

be the ratio in question, for a given indefinitely-close pair of curves of no transmission. Let the change from one of these curves to the other be made by means of any indefinitely-small changes of actual heat and of volume, δQ, δV. Then by the general equation 7, the following quantity

$$\delta F=\frac{\delta H}{Q}=\left\{\frac{1+\phi'.Q}{Q}+\frac{d^2}{dQ^2}\int P dV\right\}\delta Q+\frac{dP}{dQ}.\delta V=\frac{K_V}{kQ}.\delta Q+\frac{dP}{dQ}\delta V \quad . \quad . \quad . \quad (11.)$$

is constant for a given pair of indefinitely-close curves of no transmission, and is, therefore, the complete variation of a function, having a peculiar constant value for each curve of no transmission, represented by the following equation :—

$$F=\int\frac{dH}{Q}=\int\frac{1+\phi'.Q}{Q}dQ+\int\frac{dP}{dQ}dV. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12.)$$

This function, which I shall call a *Thermo-dynamic function*, has the following properties :—

$$H=\int Q dF \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13.)$$

is equivalent to the general equation (6.);

$$dF=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14.)$$

is the equation common to all curves of no transmission; and

$$F=\text{a given constant}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14\text{A.})$$

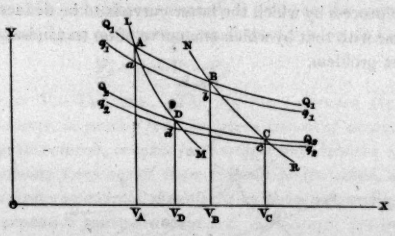
is the equation of a particular curve of no transmission.

(11.) Proposition III.—Problem. *Let it be supposed that for a given substance, the forms of all possible isothermal curves are known, but of only one curve of no transmission; it is required to describe, by the determination of points, another curve of no transmission, passing through a given point, situated anywhere out of the known curve.*

(Solution) (see fig. 7). Let LM be the known curve of no transmission; B the given point. Through B draw an isothermal curve Q_1ABQ_1, cutting LM in A. Q_1 being the quantity of heat to which this curve corresponds, draw, indefinitely near to it, the isothermal curve q_1q_1, corresponding to the quantity of heat $Q_1-\delta Q$, where δQ is an indefinitely small quantity. Draw any other pair of indefinitely close isothermal curves Q_2Q_2, q_2q_2, corresponding to the quantities of heat Q_2, $Q_2-\delta Q$; δQ being the same as before. Let D be the point where the isothermal curve Q_2Q_2 cuts the known curve of no transmission. Draw the ordinates AV_A, BV_B parallel to OY, enclosing, with the isothermal curves of Q_1 and $Q_1-\delta Q$, the small quadrilateral AB*ba*. Draw the ordinate DV_D parallel to OY, intersecting the isothermal curve of $Q_2-\delta Q$

in *d*. Lastly, draw the ordinate CV_C in such a position as to cut off from the space between the isothermal curves of Q_1 and $Q_2-\delta Q$ a quadrilateral DC*cd*, of area equal to the quadrilateral AB*ba*.

Fig. 7.



Then will C, where the last ordinate intersects the isothermal curve of Q_2, approximate indefinitely to the position of a point in the curve of no transmission passing through the given point B, when the variation of actual heat δQ is diminished without limit. And thus may be determined, to as close an approximation as we please, any number of points in the curve of no transmission NBR which passes through any given point B, when any one curve of no transmission LM is known.

(Demonstration.) For when the variation δQ diminishes indefinitely, the curves q_1q_1, q_2q_2, approach indefinitely towards the curves Q_1Q_1, Q_2Q_2 respectively; and the small quadrilaterals bounded endways by the ordinates approximate indefinitely to the small quadrilaterals bounded endways by the curves of no transmission; which latter pair of quadrilaterals are equal, by the first corollary of Proposition II.

The *symbolical expression* of this proposition is as follows:—

Let V_A, V_B, V_C, V_D be the volumes corresponding to the four points of intersection of a pair of isothermal curves with a pair of curves of no transmission; A and B being on the isothermal curve of Q_1, C and D on that of Q_2, A and D on one of the curves of no transmission, B and C on the other: then

$$\left.\begin{aligned}&\int_{V_A}^{V_B}\frac{dP}{dQ}dV\ (\text{for } Q=Q_1)=\int_{V_D}^{V_C}\frac{dP}{dQ}dV\ (\text{for } Q=Q_2)\\ \text{or}\quad &F_B-F_A=F_C-F_D\ .\ .\ .\ .\ .\ .\ .\ .\ .\end{aligned}\right\}\quad .\ .\ .\ (15.)$$

The second form of this equation is in the present case identical, because

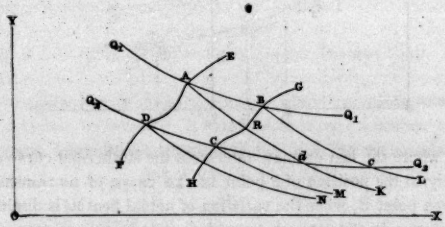
$$F_D=F_A;\ F_C=F_B.$$

(12.) Proposition IV.—Problem (see fig. 8). *The forms of all isothermal curves for a given substance being given, let* EF *be a curve of any form, representing an arbitrarily assumed succession of pressures and volumes. It is required to find, by the determination of points, a corresponding curve passing through a given point* B, *such, that*

the quantity of heat absorbed or emitted by the substance, in passing from any given isothermal curve to any other, shall be the same, whether the pressures and volumes be regulated according to the original curve EF, *or according to the curve passing through the point* B.

(Solution.) The process by which the latter curve is to be deduced from the former is precisely the same with that by which one curve of no transmission is deduced from another, in the last problem.

Fig. 8.



(Demonstration.) Let GBH be the required curve. This curve, and the curve EF, in their relation to each other, may be called *Curves of Equal Transmission.* Through B draw the isothermal curve Q_1Q_1, intersecting the curve EF in A. Draw also any other isothermal curve Q_2Q_2, intersecting EF in D and GH in C. Through A, B, C, D, respectively, draw the four indefinitely-prolonged curves of no transmission, AK, intersecting Q_2Q_2 in *d*, BL, intersecting Q_2Q_2 in *c*, CM, and DN. Conceive the whole space between the isothermal curves Q_1Q_1, Q_2Q_2, to be divided by other isothermal curves, into a series of indefinitely narrow stripes, corresponding to equal indefinitely-small variations of actual heat. Then, by the construction of the solution, the quadrilaterals cut from those stripes by the pair of curves EF, GH are all equal; and so also are the quadrilaterals cut from the stripes by the pair of curves of no transmission, AK, BL. Therefore the area ABCD is equal to the area AB*cd*. The indefinitely-prolonged areas, MCDN, L*cd*K, are evidently equal; therefore, adding this pair of equal areas to the preceding, the pair of indefinitely-prolonged areas LBAK, MCBADN are equal. Subtracting from each of these areas the part common to both, ABR, and adding to each the indefinitely-prolonged area KRCM, we find, finally, that the indefinitely-prolonged areas KADN, LBCM are equal.

But the former of those areas (by Prop. I.) represents the mechanical equivalent of the heat absorbed by the substance in passing from the actual heat Q_2 to the actual heat Q_1 through a series of pressures and volumes represented by the co-ordinates of the curve EF; and the latter, the corresponding quantity for the curve GH; therefore those curves are, with respect to each other, *Curves of Equal Transmission*, which was required

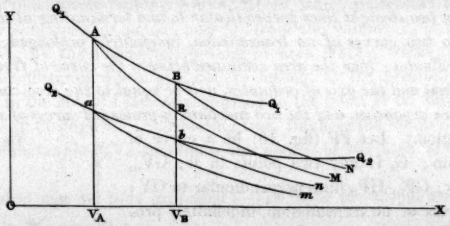
The algebraical expression of this result is that the equation (15.) holds for any pair of curves of equal transmission, as well as for a pair of curves of no transmission; or, in other terms, let F_A, F_B, F_C, F_D be the thermo-dynamic functions for the curves of no transmission passing through the four points where a pair of isothermal curves cut a pair of curves of equal transmission: A, B being on the upper isothermal curve; C, D on the lower; A, D on one curve of equal transmission, B, C on the other: then

$$F_B - F_A = F_C - F_D. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16.)$$

(13.) Proposition V.—Theorem. *The difference between the quantities of heat absorbed by a substance, in passing from one given amount of actual heat to another, at two different constant volumes, is equal to the difference between the two latent heats of expansion in passing from one of those volumes to the other, at the two different amounts of actual heat respectively, diminished by the corresponding difference between the quantities of expansive power given out.*

(Demonstration) (see fig. 9). Let Q_1Q_1 be the isothermal curve of the higher amount of actual heat; Q_2Q_2 that of the lower. Let V_A, V_B be the two given

Fig. 9.



volumes. Draw the two ordinates V_AaA, V_BbB, and the four indefinitely-prolonged curves of no transmission AM, *am*, BN, *bn*. The quantities of heat absorbed, in passing from the actual heat Q_2 to the actual heat Q_1, at the volumes V_A and V_B, are represented respectively by the indefinitely-prolonged areas MA*am*, NB*bn*. Then adding to each of those areas the indefinitely-prolonged area *nb*BAM (observing that the space below the intersection R is to be treated as negative), we find for their difference

$$\text{NB}bn - \text{MA}am = \text{NBAM} - nb\text{BA}am = (\text{NBAM} - nbam) - (\text{V}_B\text{BAV}_A - \text{V}_Bba\text{V}_A);$$

but NBAM and *nbam* represent the latent heats of expansion from V_A to V_B, at the actual heats Q_1 and Q_2 respectively; and V_BBAV_A and $V_Bba V_A$ represent the power given out by expansion from V_A to V_B at the actual heats Q_1 and Q_2 respectively; therefore the proposition is proved. Q.E.D.

This proposition, expressed symbolically, is as follows. ΔQ being the difference

of actual heat, $Q_1 - Q_2$, let $\Delta(Q+S_A)$ be the heat absorbed in passing from Q_2 to Q_1 at the volume V_A, and $\Delta(Q+S_B)$ the corresponding quantity at the volume V_B; ΔS_A and ΔS_B representing quantities of potential energy stored up in altering molecular arrangement. Then

$$\Delta(S_B - S_A) = \Delta\left(Q\frac{d}{dQ} - 1\right)\int_{V_A}^{V_B} P dV. \quad . \quad . \quad . \quad . \quad . \quad (17.)$$

(14.) *Of Curves of Free Expansion.*

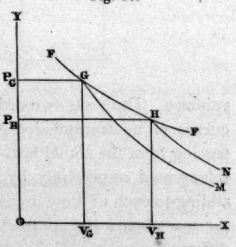
In all the preceding propositions, the whole motive power developed by an elastic substance in expanding is supposed to be communicated to external bodies; to a piston, for example, which the substance causes to move, and to overcome the resistance of a machine.

Let us now suppose that as much as possible of the motive power developed by the expansion is expended in agitating the particles of the expanding substance itself, by whose mutual friction it is finally reconverted into heat (as when compressed air escapes freely from a small orifice); and let us examine the properties of the curves which, on a diagram of energy, represent the law of expansion of the substance under these circumstances, and which may be called *Curves of free Expansion.*

(15.) Proposition VI.—Theorem. *If from two points on a curve of free expansion there be drawn two straight lines perpendicular to and terminating at the axis of ordinates, and also two curves of no transmission, indefinitely prolonged away from the origin of co-ordinates; then the area contained between the curve of free expansion, the two straight lines and the axis of ordinates, will be equal to the area contained between the curve of free expansion, and the two indefinitely-prolonged curves of no transmission.*

(Demonstration.) Let FF (fig. 10) be a curve of Free Expansion; G, H any two points in it; GV_G, HV_H ordinates; GP_G, HP_H lines perpendicular to OY; GM, HN curves of no transmission, indefinitely prolonged in the direction of X. Then the indefinitely-prolonged area MGHN represents the heat which would have to be communicated to the substance, if the motive power developed were entirely transferred to external bodies. while the area V_GGHV_H represents that motive power The excess of the rectangular area P_HHV_HO above the area P_GGV_GO, is the power necessarily given out by the elastic fluid in passing from a vessel in which the pressure is P_G and volume V_G, to a vessel in which the pressure is P_H and volume V_H. The remainder of the expansive power, represented by the area P_GGHP_H, by the mutual friction of the particles of the expanding substance, is entirely reconverted into heat, and is exactly sufficient (by the definition of the curve of free expansion) to render the communication of heat to the substance unnecessary; from which it follows, that this area is equal to the area MGHN. Q.E.D.

Fig. 10.

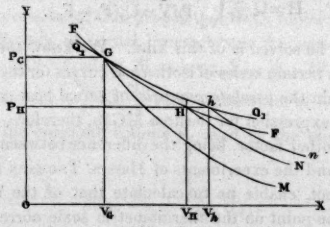


The equation of a curve of free expansion is

$$d(\Psi+PV)=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17\text{ A.})$$

(16.) *Corollary.*—In fig. 11, the same letters being retained as in the last figure, through G draw an isothermal curve Q_2Q_1, which the line P_HH produced cuts in h;

Fig. 11.



and from h draw the indefinitely-prolonged curve of no transmission, hn. Then because, by the proposition just proved, the areas P_GGHP_H and MGHN are equal, it follows that the indefinitely-prolonged area, MGhn, which represents the latent heat of expansion at the constant actual heat Q_1, from the volume V_G to the volume V_A, exceeds P_GGhP_H, by the indefinitely-prolonged area NHhn, which represents the heat which the substance would give out, in falling, at the pressure P_H, from the actual heat Q_1 to the actual heat corresponding to the point H on the curve of free expansion passing through G. Subtracting from this area the excess of the rectangle P_HV_A above the rectangle P_GV_G, we obtain the excess of the area MGhn above the area V_GGhV_A.

This conclusion may be thus expressed:—Let Q_2 be the actual heat for the point H; $\frac{K_P}{k}$ the ratio of specific heat at the constant pressure P_H to real specific heat; then

$$\left.\begin{aligned}&\int_{Q_2}^{Q_1}\frac{K_P}{k}dQ-P_HV_A+P_GV_G=\left(Q\frac{d}{dQ}-1\right)\int_{V_G}^{V_A}PdV\,(\text{for } Q=Q_1);\\ \text{otherwise:—}\quad&\int_{Q_2}^{Q_1}\frac{K_P}{k}dQ+\int_{P_H}^{P_G}VdP=Q_1(F_A-F_G). \quad . \quad . \quad . \quad .\end{aligned}\right\} \quad . \quad (18.)$$

Equation (18.) may be used, either to find points in the curve of free expansion which passes through G, when the isothermal curves and the curves of no transmission are known; or to deduce theoretical results from experiments on the form of curves of free expansion, such as those which have been for some time carried on by Mr. JOULE and Professor WILLIAM THOMSON.

Considered geometrically, these experiments give values of the area NHhn.

$$\text{The area } P_GGhP_H=\int_{P_H}^{P_G}VdP$$

is known, in each case, from previous experiments on the properties of the gas employed; and this area, by Proposition VI., is equal to the area MG*h*HN; to which adding the area NH*hn*, ascertained by experiment, we obtain the area MG*hn*, that is, the latent heat of expansion from the volume V_0 to the volume V_A, at the constant actual heat Q_1, denoted symbolically by

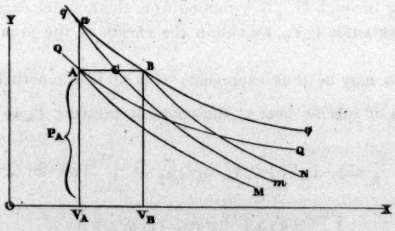
$$H=Q_1\frac{d}{dQ}\int_{V_0}^{V_A}P\,dV=Q_1(F_A-F_0).$$

Now the problem to be solved is of this kind. We know the *differences* of actual heat corresponding to a certain series of isothermal curves for the substance employed; and we have to ascertain the *absolute quantities* of actual heat corresponding to those curves. Of the above expression for the area MG*hn*, therefore, the factor Q_1 is to be determined, while the other factor, being the difference between two thermo-dynamic functions, is known; and the experiments of Messrs. Thomson and Joule, by giving the value of the product, enable us to calculate that of the unknown factor, and thence to determine the point on the thermometric scale corresponding to absolute privation of heat.

(17.) Proposition VII.—Problem. *To determine the ratio of the Apparent Specific Heats of a substance at Constant Volume and at Constant Pressure, for a given Pressure and Volume; the isothermal curves and the curves of no transmission being known.*

(Solution.) In fig. 12, let A be the point whose co-ordinates represent the given volume V_A and pressure P_A; QAQ the isothermal curve passing through A; $q\,q$ an-

Fig. 12.



other isothermal curve, very near to QQ. Through A draw the ordinate $V_A Aa$ parallel to OY, cutting qq in a; draw also AB parallel to OX, cutting qq in B. From A, a, B, draw the three indefinitely-prolonged curves of no transmission AM, am, BN.

Then the heat absorbed in passing from the actual heat Q to the actual heat q, at the constant volume V_A, is represented by the indefinitely-prolonged area MAam, while at the constant pressure P_A it is represented by the area MABN. Let the curve qq be supposed to approximate indefinitely to QQ. Then will the three-sided area AaB diminish indefinitely as compared with the areas between the curves of no transmission AM, am, BN; and consequently the area MABN will approximate in-

definitely to the sum of the areas MA*am* and *ma*BN; the ultimate ratio of which sum to the area MA*am* is therefore the required ratio of the specific heats. Now *ma*BN, as *qq* approaches QQ, approximates indefinitely to the latent heat of the small expansion $V_B - V_A$ at the actual heat Q, and this small expansion bears ultimately to the increment of pressure $P_a - P_A$, the ratio of the subtangent of the isothermal curve QQ to its ordinate at the point A.

The symbolical expression of this proposition is as follows:—Let δQ denote the indefinitely small difference of actual heat between the isothermal curves QQ, *qq*; δV the indefinitely small variation of volume $V_B - V_A$; δP the indefinitely small variation of pressure $P_a - P_A$; $\frac{K_V}{k}\delta Q$, $\frac{K_P}{k}\delta Q$ the quantities of heat required to produce the variation δQ, at the constant volume V_A, and at the constant pressure P_A respectively.

Then
$$\delta V = \frac{\delta P}{-\frac{dP}{dV}} = \frac{\frac{dP}{dQ}}{-\frac{dP}{dV}} \cdot \delta Q;$$

and
$$\frac{K_P}{k} \cdot \delta Q = \frac{K_V}{k} \cdot \delta Q + Q\frac{dP}{dQ} \cdot \delta V = \left\{ \frac{K_V}{k} + \frac{Q\left(\frac{dP}{dQ}\right)^2}{-\frac{dP}{dV}} \right\} \delta Q;$$

consequently
$$\frac{K_P}{K_V} = 1 + \frac{k}{K_V} \cdot \frac{Q\left(\frac{dP}{dQ}\right)^2}{-\frac{dP}{dV}}; \quad \ldots \ldots \quad (19.)$$

equations agreeing with equation 31 of a paper on the Centrifugal Theory of Elasticity before referred to.

(18.) *First Corollary.*—As the curves AM, *am*, BN approximate indefinitely towards parallelism, and the point *a* towards C, where *am* intersects AB, the ratio of the areas MABN : MA*am*, approximates indefinitely to that of the lines AB : AC, which are ultimately proportional, respectively, to the subtangents of the isothermal curve and the curve of no transmission passing through A. Therefore,

$$\frac{K_P}{K_V} = \frac{\text{Subtangent of Isothermal Curve}}{\text{Subtangent of Curve of No Transmission}}. \quad \ldots \ldots \quad (20.)$$

(19.) *Second Corollary.—Velocity of Sound.* The subtangents of different curves at a given point on a diagram of energy being inversely proportional to the increase of pressure produced by a given diminution of volume according to the respective curves, are inversely proportional to the squares of the respective velocities with which waves of condensation and rarefaction will travel when the relations of pressure to volume are expressed by the different curves. Therefore, if there be no sensible transmission of heat between the particles of a fluid during the passage of sound, the square of the velocity of sound must be greater than it would have been had the transmission of heat been instantaneous in the ratio of the subtangent of an isothermal curve to that

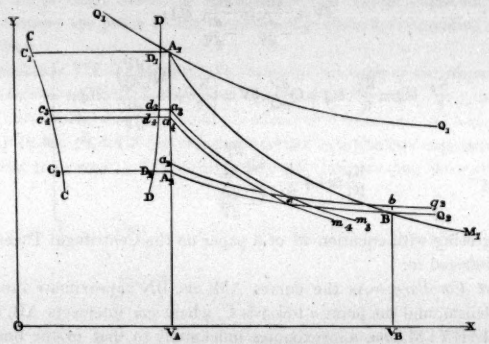
of a curve of no transmission at the same point, or of the specific heat at constant pressure to the specific heat at constant volume.

This is a geometrical proof of Laplace's law for all possible fluids. The same law is deduced from the Hypothesis of Molecular Vortices in the paper before referred to on the Centrifugal Theory of Elasticity.

(20.) Proposition VIII.—Problem. *The isothermal curves for a given substance being known, and the quantities of heat required to produce all variations of actual heat at a given constant volume; it is required to find any number of points in a curve of no transmission passing through a given point in the ordinate corresponding to that volume.*

(Solution). In fig. 13, let $V_A A_1$ be the given ordinate; $Q_1 Q_1$, $A_2 Q_2$ isothermal curves meeting it in A_1, A_2, respectively; and let it be required, for example, to find the

Fig. 13.



point where the curve of no transmission passing through A_1 intersects the isothermal curve $A_2 Q_2$. On the line $V_A A_2 A_1$, as an axis of abscissæ, describe a curve CC, whose ordinates (such as $A_2 C_2$, $a_4 c_4$, &c) are proportional to the specific heat of the substance at the constant volume V_A, and at the degrees of actual heat corresponding to the points where they are erected, divided by the corresponding rate of increase of pressure with actual heat; so that the area of this curve between any two ordinates (*e. g.* the area $a_4 c_4 c_3 a_3$) may represent the mechanical equivalent of the heat absorbed in augmenting the actual heat from the amount corresponding to the lower ordinate to that corresponding to the higher (*e. g.* from the amount corresponding to a_4 to that corresponding to a_3).

Very near to the isothermal curve $A_2 Q_2$, draw another isothermal curve $a_2 q_2$, and let the difference of actual heat corresponding to the interval between these curves be δQ. Draw a curve DD, such that the part cut off by it from each ordinate of the

curve CC shall bear the same proportion to the whole ordinate which the difference δQ bears to the whole actual heat corresponding to the ordinate; for example, let

$$\overline{A_1C_1} : \overline{A_1D_1} :: Q_1 : \delta Q$$
$$\overline{A_2C_2} : \overline{A_2D_2} :: Q_2 : \delta Q, \text{ \&c.}$$

Then draw an ordinate $V_B B b$, parallel to OY, cutting off from the space between the isothermal curves A_2Q_2, a_2q_2, a quadrilateral area A_2Bba_2 equal to $A_1D_1D_2A_2$, the area of the curve DD between the ordinates at A_1 and A_2.

Then if the difference δQ be indefinitely diminished, the point B will approximate indefinitely to the intersection required of the isothermal curve A_2Q_2 with the curve of no transmission passing through A_1; and thus may any number of points in this curve of no transmission be found.

(Demonstration.) Let A_1M_1 be the curve of no transmission required. Let a_3c_3, a_4c_4 be any two indefinitely-close ordinates of the curve CC, corresponding to the mean actual heat $Q_{3,4}$. Let a_3m_3, a_4m_4 be curves of no transmission, cutting the curves a_3q_3, A_2Q_2, so as to enclose a small quadrilateral area e. Then by the construction, and Proposition I.,

The area $a_3c_3c_4a_4$ = the indefinitely-prolonged area $m_3a_3a_4m_4$;

and by the first corollary of the second proposition and the construction,

$$\frac{\text{the area } e}{m_3a_3a_4m_4} = \frac{\delta Q}{Q_{3,4}} = \frac{\text{area } a_3d_3d_4a_4}{\text{area } a_3c_3c_4a_4}.$$

Therefore the area e = the area $a_3d_3d_4a_4$; but the area $A_1D_1D_2A_2$ is entirely made up of such areas as $a_3d_3d_4a_4$, to each of which there corresponds an equal area such as e; and when the difference δQ is indefinitely diminished the area A_2Bba_2 approximates indefinitely to the sum of all the areas such as e, that is, to equality with the area $A_1D_1D_2A_2$. Q.E.D.

The symbolical expression for this proposition is found as follows:—

$$\text{The area } A_1D_1D_2A_2 \text{ ultimately} = \delta Q . \int_{Q_2}^{Q_1} \frac{K_V}{kQ} . dQ \text{ (for } V = V_A);$$

$$\text{the area } A_2Bba_2 \text{ ultimately} = \delta Q . \int_{V_A}^{V_B} \frac{dP}{dQ} dV \text{ (for } Q = Q_2);$$

divide both sums by δQ and equate the results; then

$$\int_{V_A}^{V_B} \frac{dP}{dQ} dV \text{ (for } Q = Q_2) = \int_{Q_2}^{Q_1} \frac{K_V}{kQ} dQ \text{ (for } V = V_A), \quad . \quad . \quad . \quad . \quad (21.)$$

which denotes the equality of two expressions for the difference, $F_1 - F_2$, between the thermo-dynamic functions for the curve of no transmission A_1M, and for that passing through the point A_2.

When the relations between pressure, volume, and heat, for a given substance, are known, the equation (21.) may be transformed into one giving the volume V_B corresponding to the point at which the required curve of no transmission cuts the isothermal curve of Q_2.

Suppose, for instance, that for a perfect gas

$$PV=NQ \text{ sensibly; and } \frac{K_V}{k}=1 \text{ sensibly;} \quad . \quad . \quad . \quad (22.)$$

N being a constant (whose value for simple gases and for atmospheric air and carbonic oxide is about 0·41); then the thermo-dynamic function for a perfect gas is sensibly

$$F=\text{hyp. log } Q+N \text{ hyp. log } V; \quad . \quad . \quad . \quad . \quad . \quad . \quad (22 \text{ A.})$$

and equation (21.) gives, for the equation of a curve of no transmission,

$$\frac{V_B}{V_A}=\left(\frac{Q_1}{Q_2}\right)^{\frac{1}{N}}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23.)$$

whence

$$\frac{P_B}{P_A}=\left(\frac{V_B}{V_A}\right)^{-1-N}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24.)$$

Equations (23.) and (24.) are forms of the equation of a curve of no transmission for a perfect gas, according to the supposition of MAYER; and are approximately true for a perfect or nearly perfect gas on any supposition.

According to the hypothesis of molecular vortices, the relations between pressure, volume, and actual heat for a perfect gas are expressed by these equations:—

$$PV=NQ+h; \quad \frac{K_V}{k}=1+\frac{N^2hQ}{(NQ+h)^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (25.)$$

where h is a very small constant, which is inversely proportional to the specific gravity of the gas, and whose value, in the notation of papers on the hypothesis in question, is

$$h=Nkz, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25 \text{ A.})$$

z being the height, on the scale of a perfect gas thermometer, of the point of absolute cold above the absolute zero of gaseous tension. Hence we find, for the thermodynamic function of a perfect gas,

$$F=\text{hyp. log } Q-\frac{Nh}{NQ+h}+N \text{ hyp. log } V, \quad . \quad . \quad . \quad . \quad . \quad (26.)$$

and for the equation of a curve of no transmission,

$$\frac{V_B}{V_A}=\left(\frac{Q_1}{Q_2}\right)^{\frac{1}{N}}.e^{\left\{\frac{h}{NQ_2+h}-\frac{h}{NQ_1+h}\right\}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27.)$$

For all practical purposes yet known, these equations may be treated as sensibly agreeing with equation (23.), owing to the smallness of h as compared with NQ.

SECTION III.—OF THE EFFICIENCY OF THERMO-DYNAMIC ENGINES, WORKED BY THE EXPANSION AND CONDENSATION OF PERMANENT GASES.

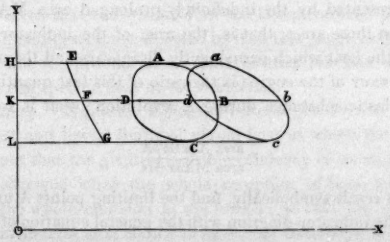
(21.) The *Efficiency* of a Thermo-dynamic Engine is the proportion of the whole heat expended which is converted into motive power; that is to say, the ratio of the motive power developed to the mechanical equivalent of the whole heat consumed.

To determine geometrically the efficiency of a thermo-dynamic engine, it is necessary to know its true indicator-diagram; that is to say, the curve whose co-ordinates represent the successive volumes and pressures which the elastic substance working the engine assumes during a complete revolution. This true indicator-diagram is not necessarily identical in figure with the diagram described by the engine on the indicator-card; for the abscissæ representing volumes in the latter diagram, include not only the volumes assumed by that portion of the elastic substance, which really performs the work by alternately receiving heat while expanding, and emitting heat while contracting, in such a manner as permanently to transform heat into motive power, but also the volumes assumed by that portion of the elastic substance, if any, which acts merely as a *cushion* for transmitting pressure to the piston, undergoing, during each revolution, a series of changes of pressure and volume, and then the same series in an order exactly the reverse of the former order, so as to transform no heat permanently to power.

The thermo-dynamic engines to be considered in the present section, are those in which the elastic substance undergoes no change of condition. We shall in the first place investigate the efficiency of those which work *without* the aid of the contrivance called an "economizer" or "regenerator," and afterwards, those which work *with* the aid of that piece of apparatus.

(22.) LEMMA.—PROBLEM. *To determine the true from the apparent indicator-diagram of a Thermo-dynamic Engine; the portion of the elastic substance which acts as a* cushion *being known, and the law of its changes of pressure and volume.*

Fig. 14.



(Solution.) In fig. 14, let *abcd* be the apparent indicator-diagram. Parallel to OX draw $\overline{Ha}$ and $\overline{Lc}$, touching this diagram in *a* and *c* respectively; then those lines

will be the lines of maximum and minimum pressure. Let $\overline{HE}$ and $\overline{LG}$ be the volumes occupied by the *cushion* at the maximum and minimum pressures respectively: draw the curve EG, such that its co-ordinates shall represent the changes of volume and pressure undergone by the cushion during a revolution of the engine. Let KF*db* be any line of equal pressure, intersecting this curve and the apparent indicator-diagram; so that $\overline{Kb}$, $\overline{Kd}$ shall represent the two volumes assumed by the whole elastic body at the pressure $\overline{OK}$, and $\overline{KF}$ the volume of the cushion at the same pressure. On this line take

$$\overline{bB}=\overline{dD}=\overline{KF};$$

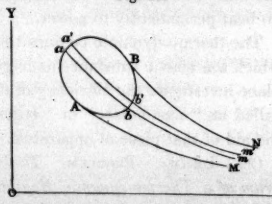
then it is evident that B and D will be two points in the true indicator-diagram; and in the same manner may any number of points be found.

The area of the true diagram ABCD is obviously equal to that of the apparent diagram *abcd*.

(23.) PROPOSITION IX.—PROBLEM. *The true indicator-diagram of a thermo-dynamic engine worked by the expansion and contraction of a substance which does not change its condition, and without a regenerator, being given, it is required to determine the efficiency of the engine.*

(Solution.) In fig. 15, let A*aa*′ B*b*′*b*A be the given true indicator-diagram. Draw two curves of no transmission, AM, BN, touching this figure at A and B respectively, and indefinitely produced towards X. Then during the process denoted by the portion A*aa*′B of the diagram the elastic substance is receiving heat, and the mechanical equivalent of the total quantity received is represented by the indefinitely-prolonged area MA*aa*′BN; during the process denoted by the portion B*b*′*b*A of the diagram, the substance is giving out heat, and the mechanical equivalent of the total heat given out is represented by the indefinitely-prolonged area MA*bb*′BN; while the difference between those areas, that is, the area of the indicator-diagram itself, represents at once the heat which permanently disappears and the motive power given out. The EFFICIENCY of the engine is the ratio of this last quantity to the total heat received by the elastic substance during a revolution; that is to say, it is denoted by the fraction,

Fig. 15.



$$\frac{\text{area A}aa'\text{B}b'b\text{A}}{\text{area MA}aa'\text{BN}}.$$

To express this result symbolically, find the limiting points A and B by combining the equation of the indicator-diagram with the general equation of curves of no transmission, viz.—

$$d\text{F}=0.$$

Then draw two indefinitely-close and indefinitely-prolonged curves of no trans-

mission, abm, $a'b'm'$, through any part of the diagram, cutting out of it a quadrilateral stripe, $abb'a'$. Let Q_1 be the mean actual heat corresponding to the upper end aa' of this quadrilateral stripe; Q_2, that corresponding to the lower end, bb'.

The area of this indefinitely-narrow stripe representing a portion of the heat converted into motive power, is found, according to the principles and notation of the third corollary to Proposition II. and of Proposition III., by multiplying the difference between the actual heats by the difference between the thermo-dynamic functions for the curves of no transmission that bound the stripe, thus :—

$$\delta E=(Q_1-Q_2)\delta F;$$

while the area of the indefinitely-prolonged stripe, $maa'm'$, representing part of the total heat expended, is, according to the same principles,

$$\delta H_1=Q_1\delta F;$$

and that of the indefinitely-prolonged stripe $mbb'm'$, representing part of the heat given out, is

$$\delta H_2=Q_2\delta F.$$

Integrating these expressions we find the following results :—

whole heat expended, $$H_1=\int_{F_A}^{F_B} Q_1 dF;$$

heat given out, $$H_2=\int_{F_A}^{F_B} Q_2 dF;$$

motive power given out, $$E=H_1-H_2=\int_{F_A}^{F_B}(Q_1-Q_2)dF;$$

efficiency, $$\frac{E}{H_1}=\frac{\int_{F_A}^{F_B}(Q_1-Q_2)dF}{\int_{F_A}^{F_B}Q_1 dF};$$

. . . . . (28.)

formulæ agreeing with equation (28.) of a paper on the Centrifugal Theory of Elasticity*; it being observed that the symbol F in the last-mentioned paper denotes, not precisely the same quantity which is denoted by it in this paper, and called a thermo-dynamic function, but the product of the part of that function which depends on the volume, by the real specific heat of the substance.

(24.) *First Corollary. Maximum Efficiency between given limits of Actual Heat.*

When the highest and lowest limits of actual heat at which the engine can work are fixed, it is evident that the greatest possible efficiency of an engine without a regenerator will be attained when the whole reception of heat takes place at the highest limit, and the whole emission at the lowest; so that the true indicator diagram is such a quadrilateral as is shown in fig. 6, and referred to in the second corollary of Proposition II.; bounded above and below by the isothermal curves denoting

* Trans. Roy. Soc. Edinb. vol. xx.

the limits of actual heat, and, laterally, by any pair of curves of no transmission. The efficiency in this case, as has been already proved in various ways, is represented by

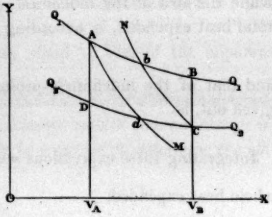
$$\frac{E}{H_1}=\frac{Q_1-Q_2}{Q_1}, \quad \ldots \ldots \ldots \ldots \quad (29.)$$

being the maximum efficiency possible between the limits of actual heat, Q_1 and Q_2.

(25.) *Second Corollary.*—PROBLEM. *To draw the diagram of greatest efficiency of a Thermo-dynamic Engine without a Regenerator, when the extent of variation of volume is limited, as well as that of the variation of actual heat.*

(Solution.) In fig. 16, let Q_1Q_1, Q_2Q_2 be the isothermal curves denoting the limits of actual heat; V_A, V_B the limits of volume. Draw the ordinates V_ADA, V_BCB, intersecting the isothermal curves in the points A, B, C, D. Through A and C respectively draw the curves of no transmission, AM cutting Q_2Q_2 in *d*, and CN cutting Q_1Q_1 in *b*. Then will A*b*C*d* be the diagram required. An analogous construction would give the diagram of greatest efficiency when the variations of pressure and of actual heat are limited; as in the Air-Engine proposed by Mr. JOULE.

Fig. 16.



(26.) *Of the use of the Economizer or Regenerator in Thermo-dynamic Engines.*

As the actual heat of the elastic substance which works a Thermo-dynamic Engine requires to be alternately raised and lowered, it is obvious that unless these operations are performed entirely by compression and expansion, without reception or emission of heat (as in the case of maximum efficiency described in the first corollary of Proposition IX.), part, at least, of the heat emitted during the lowering of the actual heat may be stored up, by being communicated to some solid conducting substance, and used again by being communicated back to the elastic substance, when its actual heat is being raised. The apparatus used for this purpose is called an Economizer or Regenerator, and was first invented, about 1816, by the Rev. ROBERT STIRLING. In the Air-Engine proposed by him, it consisted of a sheet-metal plunger surrounded by a wire grating or network; in that of Mr. JAMES STIRLING, it is composed of thin parallel plates of metal or glass through which the air passes longitudinally, and in the engine of Captain ERICSSON, of several sheets of wire gauze.

A regenerator may be regarded as consisting of an indefinite number of strata, with which the elastic substance is successively brought into contact; each stratum serving to store up and give out the heat required to produce one particular indefinitely small variation of the actual heat of the working substance.

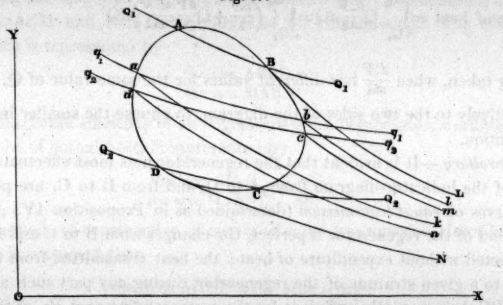
A *perfect regenerator* is an ideal apparatus of this kind, in which the mass of material is so large, the surface exposed so extensive, and the conducting powers so

great, as to enable it to receive and emit heat instantaneously without there being any sensible difference of temperature between any part of the regenerator and the contiguous portion of the working substance; and from which no appreciable amount of heat is lost by conduction or radiation. In theoretical investigations it is convenient, in the first place, to determine the saving of heat effected by a perfect regenerator, and afterwards to make allowance for the losses arising from the non-fulfilment of the conditions of ideally perfect action; losses which, in the present imperfect state of our knowledge of the laws of the conduction of heat, can be ascertained by direct experiment only *.

(27.) PROPOSITION X.—PROBLEM. *The true indicator-diagram of any thermo-dynamic engine being given, to determine the amount of heat saved by a perfect regenerator.*

(Solution.) Let ABCD (in fig. 17) be the given indicator-diagram. Across it draw any two indefinitely-close isothermal curves; q_1q_1 intersecting it in a, b; and q_2q_2 intersecting it in d, c. To the stripe between those two curves, speaking generally,

Fig. 17.



a certain layer or stratum of the regenerator corresponds, which receives heat from the working substance during the change from b to c, and restores the same amount of heat during the change from d to a. The amount of heat economized by the layer in question is thus found. Through the four points a, b, c, d, draw the indefinitely-prolonged curves of no transmission, ak, bl, cm, dn; then the smaller of the two indefinitely-prolonged areas, $lbcm$, $kadn$, represents the heat saved by the layer of the regenerator corresponding to the indefinitely-narrow stripe between the isothermal curves q_1q_1 and q_2q_2.

Draw two curves of no transmission, BL, DN, touching the diagram; and through

* It is true that the problem of the waste of heat in the action of the regenerator is capable of a hypothetical solution by the methods of FOURIER and POISSON; and I have by these methods obtained formulæ which are curious in a mathematical point of view; but owing to our ignorance of the absolute values and laws of variation of the coefficients of conductivity contained in these formulæ, they are incapable of being usefully applied; and I therefore for the present refrain from stating them.

the points of contact, B and D, draw the isothermal curves, Q_1Q_1 cutting the diagram in A and B, and Q_2Q_2 cutting it in C and D. Then because, during the whole of the change from D through A to B, the working substance is receiving heat, and during the whole of the change from B through C to D, emitting heat, the regenerator can have no action above the isothermal curve Q_1Q_1, nor below the isothermal curve Q_2Q_2.

The whole of the diagram between these curves is to be divided by indefinitely-close isothermal curves into stripes like *abcd*; and the saving of heat effected by the layer of the regenerator corresponding to each stripe ascertained in the manner described, when the whole saving may be found by summation or integration.

The symbolical expression of this result is as follows. Let the points of contact, B, D, which limit the action of the regenerator, and the corresponding quantities of actual heat, Q_1, Q_2, be found, as in Proposition IX., by means of the equation $dF=0$.

Then

$$\text{the saving of heat} = \int_{Q_2}^{Q_1} Q \frac{d.F}{dQ} dQ = \int_{Q_2}^{Q_1} \left(\frac{K_V}{k} + Q \frac{dP}{dQ} \cdot \frac{d.V}{dQ} \right) dQ \quad . \quad . \quad . \quad . \quad . \quad . \quad (30.)$$

care being taken, when $\frac{d.F}{dQ}$ has different values for the same value of Q, corresponding respectively to the two sides of the diagram, to choose the smaller in performing the integration.

(28.) *Corollary.*—It is evident that the regenerator acts most effectually, when the outlines of the indicator-diagram from A to D, and from B to C, are portions of a pair of curves of *equal transmission* (determined as in Proposition IV.); for then, if the operation of the regenerator is perfect, the changes from B to C and from D to A will be effected without expenditure of heat; the heat transmitted from the working substance to a given stratum of the regenerator, during any part such as *bc*, of the operation BC, being exactly sufficient for the corresponding part, *da*, of the operation DA. In this case $\frac{d.F}{dQ}$ for each value of Q between Q_1 and Q_2, has the same value at either side of the diagram.

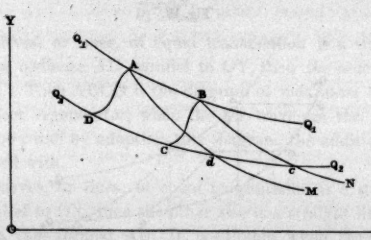
In fact, the effect of a perfect regenerator is, to confer upon any pair of curves of *equal transmission* the properties of a pair of curves of *no transmission*.

(29.) PROPOSITION XI.—THEOREM. *The greatest efficiency of a thermo-dynamic engine, working between given limits of actual heat, with a perfect regenerator, is equal to the greatest efficiency of a thermo-dynamic engine, working between the same limits of actual heat, without a regenerator.*

(Demonstration.) In fig. 18, let Q_1Q_1, Q_2Q_2 be the isothermal curves denoting the given limits of actual heat. Let AD, BC be a pair of curves of equal transmission of any form. Then by the aid of a perfect regenerator, the whole of the heat given out by the elastic substance during the operation BC may be stored up, and given

out again to that substance in such a manner as to be exactly sufficient for the operation DA; so that the whole consumption of heat in one revolution by an engine

Fig. 18.



whose indicator-diagram is ABCD, may be reduced simply to the latent heat of expansion during the operation AB, which is represented by the indefinitely-prolonged area MABN, A*d*M and B*c*N being curves of no transmission. The efficiency of such an engine is represented by

$$\frac{\text{the area ABCD}}{\text{the area MABN}}.$$

Now the maximum efficiency of an engine without a regenerator, working between the same limits of actual heat, is represented by

$$\frac{\text{the area AB}cd}{\text{the area MABN}}=\frac{Q_1-Q_2}{Q_1};$$

and from the mode of construction of curves of equal transmission, described in Proposition IV., it is evident that

$$\text{the area ABCD}=\text{the area AB}cd;$$

hence the maximum efficiencies, working between the given limits of actual heat, Q_1 and Q_2, are equal, with or without a perfect regenerator. Q.E.D.

(30.) *Advantage of a Regenerator.*

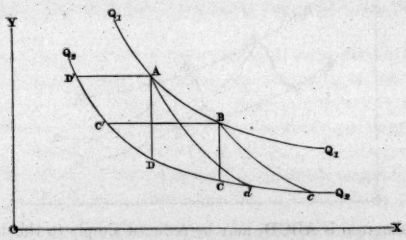
It appears from this theorem that the advantage of a regenerator is, not to increase the maximum efficiency of a thermo-dynamic engine between given limits of actual heat, but to enable that amount of efficiency to be attained with a less amount of expansion, and consequently with a smaller engine.

Suppose, for instance, that to represent the isothermal curves, and the curves of no transmission, for a gaseous substance, we adopt the approximate equations already given in article 20, viz.—

$$\left.\begin{aligned}&\text{for the isothermal curve of Q, } PV=NQ;\\&\text{for a curve of no transmission } \frac{V_2}{V_1}=\left(\frac{Q_2}{Q_1}\right)^{-\frac{1}{N}}=\left(\frac{P_2}{P_1}\right)^{\frac{-1}{1+N}};\end{aligned}\right\} \quad \ldots \quad (31.)$$

and let us compare the forms of the indicator-diagrams without and with a regenerator, for a perfect air-engine, working between given limits as to actual heat, defined by the isothermal curves Q_1Q_1, Q_2Q_2 in fig 19.

Fig. 19.



The amount of expansion at the higher limit of heat being arbitrary, let us suppose it to be from the volume V_A to the volume V_B, corresponding respectively to the points A and B, and to be the same in all cases, whether with or without a regenerator.

The engine being without a regenerator, the diagram corresponding to the maximum efficiency has but one form, viz. ABc*d*, where Bc, A*d* are curves of no transmission. Hence, in this case, there must be an additional expansion, from the volume V_B to the volume

$$V_c = V_B \cdot \left(\frac{Q_1}{Q_2}\right)^{\frac{1}{N}}, \quad \ldots \ldots \ldots \ldots \quad (32.)$$

for the purpose merely of lowering the actual heat of the air without loss of heat; and the engine must be made large enough to admit of this expansion, otherwise heat will be wasted.

On the other hand, if the engine be provided with a perfect regenerator, any pair of curves of equal transmission passing through A and B will complete a diagram of maximum efficiency. The property of a pair of these curves being, as shown in Proposition IV., that the difference of their thermo-dynamic functions,

$$\Delta F \left(= \int \frac{dP}{dQ} dV \text{ when } Q \text{ is constant} \right),$$

is the same for every value of Q, it follows, that for a gas, according to the approximate equation (23.), the property of a pair of curves of equal transmission is, that the volumes corresponding to the intersections of the two curves by the same isothermal curve, are in a ratio which is the same for every isothermal curve. Thus let V_a, V_b be such a pair of volumes, then this equation

$$\frac{V_b}{V_a} = \frac{V_B}{V_A} \quad \ldots \ldots \ldots \ldots \quad (33.)$$

defines a pair of curves of equal transmission. From this and from equation (31.), it follows, that for such a pair of curves

$$\frac{P_b}{P_a}=\frac{P_B}{P_A}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34.)$$

If one of the curves, or lines, of equal transmission is a straight line of equal volumes, that is, an ordinate AD parallel to OY, then the other is an ordinate BC, parallel to OY also. Then ABCD is the diagram of maximum efficiency for an air-engine with a perfect regenerator, when the air traverses the regenerator without alteration of volume; and by adopting this diagram, the additional expansion from V_B to V_c is dispensed with.

If one of the curves, or lines, of equal transmission is a straight line of equal pressures AD' parallel to OX, then the other also is a straight line of equal pressures BC'. The diagram thus formed, ABC'D', is suitable, when the air, as in Ericsson's engine, has to traverse the regenerator without change of pressure.

It must be observed, that no finite mass, or extent of conducting surface, will enable a regenerator to act with the ideal perfection assumed in Propositions X. and XI., and their corollaries.

Owing to the want of a general investigation of the theory of the action of the regenerator based on true principles, those who have hitherto written respecting it have either exaggerated its advantages or unduly depreciated them. From this remark, however, must be excepted a calculation of the expenditure of heat in Captain Ericsson's engine, by Professor Barnard of the University of Alabama*.

(31.) *General Remarks on the preceding Propositions.*

The eleven preceding propositions, with their corollaries, are the geometrical representation of the theory of the mutual transformation of heat and motive power, by means of the changes of volume of a homogeneous elastic substance which does not change its condition. All these propositions are virtually comprehended in the first two, of which, perhaps, the most simple enunciations are the following:—

I. The mechanical equivalent of the heat absorbed or given out by a substance in passing from one given state as to pressure and volume to another given state, through a series of states represented by the co-ordinates of a given curve on a diagram of energy, is represented by the area included between the given curve and two curves of no transmission of heat drawn from its extremities, and indefinitely prolonged in the direction representing increase of volume.

II. If across any pair of curves of no transmission on a diagram of energy there be drawn any series of isothermal curves at intervals corresponding to equal differences of actual heat, the series of quadrilateral areas thus cut off from the space between the curves of no transmission will be all equal to each other.

These two propositions are the necessary consequences of the definitions of iso-

* Silliman's Journal, September 1853.

thermal curves and curves of no transmission on a diagram of energy, and are the geometrical representation of the application to the particular case of heat and expansive power, of two axioms respecting Energy in the abstract, viz.—

I. The sum of Energy in the Universe is unalterable.

II. The effect, in causing Transformation of Energy, of the whole quantity of Actual Energy present in a substance, is the sum of the effects of all its parts.

The application of these Axioms to Heat and Expansive Power virtually involves the following Definition of Expansive Heat:—

Expansive Heat is a species of Actual Energy, the presence of which in a substance affects, and in general increases, its tendency to expand.

And this definition, arrived at by induction from experiment and observation, is the foundation of the theory of the expansive action of heat.

Section IV.—Of Temperature, the Mechanical Hypothesis of Molecular Vortices, and the Numerical Computation of the Efficiency of Air-Engines.

(32.) In order to apply the propositions of the preceding articles to existing substances, besides experimental data sufficient for the determination, direct or indirect, of the isothermal curves and curves of no transmission, it is necessary also to know the relation, for the substance in question, between the quantity of heat actually present in it under any circumstances, and its *Temperature*; a quantity measured by the product of the pressure, volume, and specific gravity of a mass of perfect gas, when in such a condition that it has no tendency to communicate heat to, or to abstract heat from, the substance whose temperature is ascertained.

The nature of the relation between heat and temperature has been discussed in investigations already published, as a consequence deducible from a hypothesis respecting the molecular constitution of matter, with the aid of data supplied by the experiments of Messrs. Thomson and Joule and of M. Regnault. Nevertheless it seems to me desirable to add here a few words respecting the grounds, independent of direct experiment, for adopting the hypothesis of molecular vortices as a probable conjecture, the extent to which, by the aid of this hypothesis, the results of experiment were anticipated, and its use, in conjunction with the results of experiment, as a means of arriving at a knowledge of the true law of the relation between temperatures and total quantities of heat.

To introduce a hypothesis into the theory of a class of phenomena, is to suppose that class of phenomena to be, in some way not obvious to the senses, constituted of some other class of phenomena with whose laws we are more familiar. In thus framing a hypothesis, we are guided by some analogy between the laws of the two classes of phenomena: we conclude, from this analogy of laws, that the phenomena themselves are probably alike. This act of the mind is the converse of the process of ordinary physical reasoning; in which, perceiving that phenomena are alike, we conclude that their laws are analogous. The results, however, of the latter process

of reasoning may be certainly true, while those of the former can never be more than probable; for how complete soever the analogy between the laws of two classes of phenomena may be, there will always remain a possibility of the phenomena themselves being unlike. A hypothesis, therefore, is incapable of absolute proof; but the agreement of its results with those of experiment may give it a high degree of probability.

The laws of the transmission of radiant heat are analogous to those of the propagation of a transverse oscillatory movement. The laws of thermometric heat are analogous to those of motion, inasmuch as both are convertible into mechanical effect; and motion, especially that of eddies in liquids and gases, is directly convertible into heat by friction. If, guided by these analogies, we assume as a probable hypothesis that heat consists in some kind of molecular motion, we must suppose that thermometric heat is such a molecular motion as will cause bodies to tend to expand; that is to say, a motion productive of centrifugal force. Thus we are led to the hypothesis of Molecular Vortices.

This hypothesis, besides the principles already enunciated, of the mutual transformation of heat and motive power in homogeneous substances, leads to the following special conclusion respecting the

Relation between Temperature and Actual Heat:—

When the temperature of a substance, as measured by a perfect-gas thermometer, rises by equal increments, the actual heat present in the substance rises also by equal increments:—

a principle expressed symbolically by the equation

$$Q = k(\tau - \varkappa), \quad \ldots \ldots \ldots \quad (35.)$$

where Q is the actual heat in unity of weight of a substance, τ its temperature, measured from the absolute zero of gaseous tension, $\varkappa$ the temperature of absolute cold, measured from the same point, and k the real specific heat of the substance, expressed in terms of motive power*.

The enunciation of this law was originally an anticipation of the results of experiment; for when it appeared, no experimental data existed by which its soundness could be tested.

Since then, however, one confirmation of this law has been afforded by the experiments of M. Regnault, showing that the specific heat of atmospheric air is sensibly constant at all temperatures and at all densities throughout a very great range; and another, by the experiments of Messrs. Joule and Thomson referred to in Proposition VI., on the thermic phenomena of gases rushing through small apertures, which not only verify the theoretical principle, but afford the means of computing approximately the position $\varkappa$ of the point of absolute cold on the thermometric scale.

* The hypothesis of Mayer amounts to supposing that $\varkappa = 0$, or that the zero of gaseous tension coincides with the point of absolute cold.

According to this relation between temperature and heat, every isothermal curve on a diagram of energy is also a curve of equal temperature. The isothermal curve, for example, corresponding to a constant quantity of actual heat, Q, corresponds also to a constant absolute temperature,

$$\tau=\frac{Q}{k}+\varkappa. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36.)$$

The curve of absolute cold is that of the absolute temperature $\varkappa$.

Any series of isothermal curves at intervals corresponding to equal differences of heat, correspond to a series of equidistant temperatures.

Hence we deduce

PROPOSITION XII.—THEOREM. *Everything that has been predicated, in the propositions of the preceding articles, of the mutual proportions of quantities of actual heat and their differences, may be predicated also of the mutual proportions of temperatures as measured from the point of absolute cold, and their differences.*

The symbolical expression of this theorem is, that in all the equations of the preceding sections, we may make the following substitutions :—

$$\frac{Q_2}{Q_1}=\frac{\tau_2-\varkappa}{\tau_1-\varkappa}; \quad \frac{(\Delta, \delta, \text{or } d)Q}{Q}=\frac{(\Delta, \delta, \text{or } d)\tau}{\tau-\varkappa}. \quad . \quad . \quad . \quad . \quad (36\text{ A.})$$

This theorem is not, like those which have preceded it, the consequence of a set of definitions. It is a law known by induction from experiment, aided by a hypothesis or conjecture with the results of which those of experiment have been found to agree.

It is true that the theorem itself might have been stated in the form of a definition of degrees of temperature ; but then induction from experiment would still have been required, to prove that temperature, as measured in the usual way, agrees with the definition.

By substituting symbols according to the above theorem, and making

$$\varphi.Q=f.\tau,$$

the general equation of the expansive action of heat is made to take the following form :—

$$\Delta.\Psi=\Delta.H-\int PdV=\Delta Q+\Delta.S=k.\Delta\tau+\Delta f.\tau+\int\left\{(\tau-\varkappa)\frac{dP}{d\tau}-P\right\}.dV, \quad . \quad (37.)$$

which agrees with the equation deduced directly from the hypothesis of molecular vortices, if we admit that

$$\left.\begin{aligned} f.\tau&=kN\varkappa\left(\text{hyp. log }\tau+\frac{\varkappa}{\tau}\right)\\ \text{and consequently}\quad f'.\tau&=kN.\left(\frac{\varkappa}{\tau}-\frac{\varkappa^2}{\tau^2}\right). \quad . \quad . \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (37\text{ A.})$$

The differential form of equation (37.) is

$$d.\Psi=d.H-PdV=dQ+d.S=K_\tau d\tau+\left\{(\tau-\varkappa)\frac{dP}{d\tau}-P\right\}dV, \quad . \quad . \quad . \quad (38.)$$

where $$K_v = k + f'.\tau + (\tau - \varkappa)\int \frac{d^2P}{d\tau^2}.dV.$$

The expression for the Thermo-dynamic function denoted by F takes the form

$$F = \int \frac{1 + \frac{1}{k}.f'.\tau}{\tau - \varkappa}.d\tau + \frac{1}{k}\int \frac{dP}{d\tau}.dV; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39.)$$

but a more convenient thermo-dynamic function, bearing the same relation to temperature as reckoned from the point of absolute cold, which the function F does to actual heat, is formed by multiplying the latter by the real specific heat k, thus:—

$$\Phi = kF = \int \frac{k + f'.\tau}{\tau - \varkappa}d\tau + \int \frac{dP}{d\tau}dV, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40.)$$

which, being introduced into the general equation, transforms it to

$$\Delta.\Psi = \int (\tau - \varkappa)d\Phi - \int P dV. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40\,\text{A}.)$$

(33.) *Of the Numerical Computation of the Efficiency of Air-Engines, with or without a perfect Regenerator.*

The relation between temperature and heat being known, the preceding propositions can be applied to determine the efficiency, and other circumstances relative to the working of Thermo-dynamic engines. To exemplify this application of the theory, let the substance working the engine be atmospheric air, and let the real indicator-diagram be such as to develope the maximum efficiency between two given absolute temperatures τ_1 and τ_2, being a quadrilateral, as in fig. 19, of which two sides are portions of the isothermal curves of those temperatures, and the other two, portions of a pair of curves of equal transmission, of such a form as may be best suited to the easy working of the engine. Should these curves be curves of no transmission, a regenerator may be dispensed with. In every other case a regenerator is necessary, to prevent waste of heat; and for the present its action will be assumed to be perfect, as the loss which occurs from its imperfect action cannot be ascertained except by direct experiment.

In this investigation it is unnecessary to use formulæ of minute accuracy; and for practical purposes, those will be found sufficient which treat air as a perfect gas, whose thermometric zero of pressure coincides with the point of absolute cold, viz.—

$$\left.\begin{array}{l} 272°\tfrac{1}{2} \text{ Centigrade, or} \\ 490°\tfrac{1}{2} \text{ Fahrenheit,} \end{array}\right\} \text{below melting ice;}*$$

* This estimate of the position of the point of absolute cold is to be considered as merely approximate, recent experiments and calculations having shown that it may possibly be too high by about 1½° Centigrade. It is, however, sufficiently correct for all practical purposes.—W. J. M. R., June 1854.

whose real specific heat is equal to its specific heat at constant volume, being

$$\mathfrak{k}=K_V=\begin{cases}234{\cdot}6 \text{ feet of fall per Centigrade degree, or}\\ 130{\cdot}3 \text{ feet of fall per degree of Fahrenheit;}\end{cases}$$

whose specific heat at constant pressure (as determined by M. REGNAULT) is $0{\cdot}238\times$ the specific heat of liquid water, or

$$K_P=\begin{cases}330{\cdot}8 \text{ feet of fall per Centigrade degree, or}\\ 183{\cdot}8 \text{ feet of fall per degree of Fahrenheit;}\end{cases}$$

the ratio of these two quantities being

$$\frac{K_P}{K_V}=1+N=1{\cdot}41,$$

as calculated from the velocity of sound.

The volume occupied by an avoirdupois pound of air, at the temperature of melting ice, under the pressure of one pound on the square foot, as calculated from the experiments of M. REGNAULT, is

$$P_0V_0=26214{\cdot}4 \text{ cubic feet.}$$

This represents also the length in feet of a column of air of uniform density and sectional area, whose weight is equal to its elastic pressure on the area of its section at the temperature of melting ice.

It will be found convenient, in expressing the temperature, as measured from the point of absolute cold, to make the following substitution:—

$$\tau-\varkappa=T+T_0, \quad \ldots\ldots\ldots \quad (41.)$$

where T represents the temperature as measured on the ordinary scale from the temperature of melting ice, and T_0 the height of the temperature of melting ice above the point of absolute cold, as already stated.

Then we have $$N\mathfrak{k}=\frac{P_0V_0}{T_0}. \quad \ldots\ldots\ldots \quad (41\,A.)$$

According to these data, the equation of the isothermal curve of air for any temperature T is

$$PV=P_0V_0.\frac{T+T_0}{T_0}=N\mathfrak{k}(T+T_0). \quad \ldots\ldots \quad (42.)$$

The thermo-dynamic functions are—

$$\left.\begin{aligned}&\text{for quantities of actual heat,} \quad F=\text{hyp. log } Q+N \text{ hyp. log } V;\\ &\text{for temperatures,} \quad \Phi=\mathfrak{k}F+\text{constant}=K_V\{\text{hyp. log } (T+T_0)+N \text{ hyp. log } V\}\\ &\qquad\qquad =K_V \text{ hyp. log } (T+T_0)+\frac{P_0V_0}{T_0}.\text{hyp. log } V;\end{aligned}\right\} \quad (42\,A.)$$

consequently the equation of any curve of no transmission is

$$\left.\begin{array}{c}\Phi = \text{constant; otherwise} \\ (T+T_0).V^N = \text{const.; or } P.V^{1+N} = \text{const.; or} \\ (T+T_0).P^{\frac{N}{1+N}} = \text{constant;}\end{array}\right\} \quad . \quad . \quad . \quad . \quad (43.)$$

in which $N = 0{\cdot}41$, $1+N = 1{\cdot}41$, $\frac{N}{1+N} = 0{\cdot}2908$.

The maximum possible efficiency between any two temperatures T_1 and T_2 is given by the universal formula,

$$\frac{E}{H_1} = \frac{H_1 - H_2}{H_1} = \frac{T_1 - T_2}{T_1 + T_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44.)$$

The latent heat of expansion of unity of weight of air at a given constant temperature T_1, from the volume V_A to the volume V_B, is sensibly equivalent simply to the expansive power developed, being given by the following formula :—

$$H_1 = (T_1+T_0).(\Phi_B - \Phi_A) = P_0 V_0 . \frac{T_1+T_0}{T_0} . \text{hyp. log} \frac{V_B}{V_A} = \int_{V_A}^{V_B} P dV. \quad . \quad . \quad (45.)$$

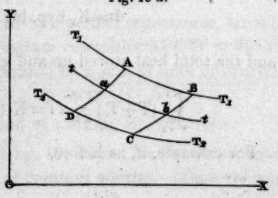
Let V_a and V_b be the volumes corresponding to the points at which any isothermal curve intersects a given pair of curves of no transmission, or of equal transmission; then the ratio of these volumes,

$$\frac{V_b}{V_a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46.)$$

is constant for every such pair of points on the given pair of curves; because the difference of the thermo-dynamic functions, which is proportional to the logarithm of this ratio, is constant.

Hence, if in fig. 19 A, two isothermal curves, T_1T_1, T_2T_2, be the upper and lower boundaries of an indicator-diagram of maximum energy for an air-engine, A*a*D an arbitrary curve bounding the diagram at one side, and B the other limit of the expansion at the higher temperature; the fourth boundary, being a curve of equal transmission to A*a*D, may be described by this construction; draw any isothermal curve *tt* cutting A*a*D in *a*, and make

Fig. 19 A.



$$V_A : V_B :: V_a : V_b, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47.)$$

then will *b* be a point in the curve sought, B*b*C.

Suppose, for example, that the form assumed for A*a*D is a hyperbola, concave towards OY, and having the following equation,—

$$P_a=\frac{\alpha}{\beta-V_a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47\text{ A.})$$

in which α and β are two arbitrary constants; and let the ratio $\frac{V_B}{V_A}=r$.

Then must the curve B*b*C be another hyperbola concave towards OY, having for its equation

$$P_b=\frac{\alpha}{r\beta-V_b}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47\text{ B.})$$

The total expenditure of heat, per pound of air per stroke, in a perfect air-engine, is the latent heat of expansion from V_A to V_B, given by equation (45.).

The heat to be abstracted by refrigeration is the latent heat of compression from V_C to V_D; and is found by substituting in the same equation, the lower temperature T_2 for the higher temperature T_1.

The indicated work, per pound of air per stroke, being the difference between those two quantities, is found by multiplying the range of temperature by the difference of the thermo-dynamic functions Φ for the curves AD, BC, or by multiplying the latent heat of expansion by the efficiency, and has the following value:—

$$E=H_1-H_2=(T_1-T_2).(\Phi_B-\Phi_A)=P_0V_0.\frac{T_1-T_2}{T_0}.\text{hyp. log}\frac{V_B}{V_A}. \quad . \quad . \quad . \quad (48.)$$

The heat alternately stored up and given out by the regenerator (supposing it to work perfectly) is to be computed as follows. Let the arbitrary manner in which volume is made to vary with temperature, on either of the curves D*a*A, C*b*B, be expressed by an equation

$$V=\Psi.T,$$

then the thermo-dynamic function Φ takes the form

$$\Phi=K_V\,\text{hyp. log}\,(T+T_0)+\frac{P_0V_0}{T_0}\,\text{hyp. log}\,\Psi.T;$$

and the total heat stored up and given out, per pound of air per stroke, is

$$\int_{T_2}^{T_1}(T+T_0)\frac{d.\Phi}{dT}dT=K_V(T_1-T_2)+\frac{P_0V_0}{T_0}\int_{T_2}^{T_1}\frac{(T+T_0)\Psi'.T}{\Psi.T}dT. \quad . \quad . \quad . \quad . \quad (49.)$$

For example, if, as before,

$$P_a=\frac{\alpha}{\beta-V_a}$$

be the equation of the curve DA, then

$$V_a=\frac{\beta(T+T_0)}{T+T_0\left(1+\frac{\alpha}{P_0V_0}\right)},$$

and the heat stored up, per pound of air per stroke, is

$$K_v(T_1-T_2)+\alpha.\text{hyp. log}\left\{\frac{T_1+T_0\left(1+\frac{\alpha}{P_0V_0}\right)}{T_2+T_0\left(1+\frac{\alpha}{P_0V_0}\right)}\right\} \quad . \quad . \quad . \quad . \quad . \quad (49\text{ A.})$$

(33 A.) *Numerical Examples.*

To illustrate the use of these formulæ, let us take the following example:—

Temperature of receiving heat, $T_1=343°{\cdot}3$ Centigrade.

$T_1+T_0=615°{\cdot}8$ Centigrade.

Temperature of emitting heat, $T_2=35°{\cdot}4$ Centigrade.

$T_2+T_0=307°{\cdot}9$ Centigrade.

Ratio of Effective Expansion, $\frac{V_B}{V_A}=\frac{V_C}{V_D}=\frac{P_A}{P_B}=\frac{P_D}{P_C}=\frac{3}{2}$.

From these data are computed the following results:—

Maximum Efficiency,—

$$\frac{307°{\cdot}9}{615°{\cdot}8}=\frac{1}{2}.$$

Heat expended, or latent heat of expansion,—

$H_1=P_0V_0\times\frac{615.8}{272{\cdot}5}\times\text{hyp. log}\frac{3}{2}=24020$ foot-pounds per pound of working air per stroke.

Heat abstracted by refrigeration,—

$H_2=P_0V_0\times\frac{307{\cdot}9}{272{\cdot}5}\times\text{hyp. log}\frac{3}{2}=12010$ foot-pounds per pound of working air per stroke.

Work performed,—

$H_1-H_2=P_0V_0\times\frac{307{\cdot}9}{272{\cdot}5}\times\text{hyp. log}\frac{3}{2}=12010$ foot-pounds per pound of working air per stroke.

To exemplify the computation of the heat stored by a perfect regenerator, let it be supposed, in the first place, that the indicator-diagram resembles ABC'D' in fig. 19, where the curves of equal transmission are represented by a pair of lines of constant pressure. Then the heat to be stored is

$K_p(T_1-T_2)=101{,}800$ foot-pounds per pound of working air per stroke.

Secondly, let the diagram resemble ABCD in fig. 19, where the curves of equal transmission are represented by a pair of lines of constant volume. Then the heat to be stored is

$K_v(T_1-T_2)=72{,}233$ foot-pounds per pound of working air per stroke.

Thirdly, let the curves of equal transmission, as in a recent example, be hyperbolas, concave towards OY, and let the arbitrary constant α have the following value,—

$\alpha=P_0V_0=26214{\cdot}4$ foot-pounds;

then the heat to be stored, according to equation (49 A.), is

$$72{,}233+26214{\cdot}4\times\text{hyp. log}\frac{888{\cdot}3}{580{\cdot}4}=72{,}233+11{,}157$$

$$=83{,}390 \text{ foot-pounds per pound of working air per stroke.}$$

The large proportions borne by these quantities to the whole heat expended, show the importance of efficient action in the regenerator to economy of fuel. The quantity of heat to be stored, however, becomes smaller, as the curves of equal transmission approach those of no transmission, for which it is null. The additional expansion requisite in this last case is found by the following computation,—

$$\frac{V_C}{V_B}=\frac{V_D}{V_A}=\left(\frac{T_1+T_0}{T_2+T_0}\right)^{\frac{1}{N}}=2^{\frac{1}{0{\cdot}41}}=5{\cdot}423,$$

the result of which shows the great additional bulk of engine required, in order to obtain the maximum efficiency without a regenerator.

Supposing one pound of coal, by its combustion, to be capable of communicating heat to the air working in an engine corresponding with the above example, to an amount equivalent to

6,000,000 foot-pounds

(an amount which would evaporate about 7 lbs. of water), the maximum theoretical duty of one pound of such coal in such an engine, without waste of heat or power, would be

3,000,000 foot-pounds,

corresponding to

$\frac{3{,}000{,}000}{12{,}010}=249$ strokes of a pound of working air, with the effective expansion $\frac{3}{2}$.

The deductions to be made from this result in practice must of course be determined by experience.

Section V.—Propositions relative to a heterogeneous mass, or aggregate, especially in vapour-engines.

(34.) The Heterogeneous Mass to which the present investigation refers, is to be understood to mean an Aggregate of portions of different ingredients, in which each ingredient occupies a space, or a number of spaces, of sensible magnitude.

The results arrived at are not applicable to mixtures in which there is a complete mutual diffusion of the molecules of the ingredients, so that every space of appreciable magnitude contains every ingredient in a fixed proportion. A mixture of this kind, when the relations between its pressure, volume, heat, and temperature are known, may be treated, so far as regards the expansive action of heat, as a homogeneous substance.

The ingredients of an aggregate are heterogeneous with respect to the expansive

action of heat, when either their specific heats, or their volumes for unity of weight at a given pressure and temperature, or both these classes of quantities, are different.

Hence a portion of a liquid, and a portion of its vapour, enclosed in the same vessel, though chemically identical and mutually transformable, are heterogeneous, and are to be treated as an aggregate, with respect to the expansive action of heat.

M. Clausius and Professor William Thomson have applied their formulæ to the aggregate composed of a liquid and its vapour, and have pointed out certain relations which must exist between the pressure and density of a liquid and its vapour, and the latent heat of evaporation.

I shall now apply the geometrical method of this paper to the theory of the expansive action of heat in an aggregate, especially that consisting of a liquid and its vapour. The total volumes are, for the present, supposed not to be large enough to exhibit any appreciable differences of pressure due to gravitation.

(35.) Proposition XIII.—Theorem. *In an aggregate in equilibrio, the pressure of each ingredient must be the same; and the quantity of heat in unity of weight of each ingredient must be inversely proportional to its real specific heat; that is to say, the temperature must be equal.*

The following is the symbolical expression of this theorem, with certain conclusions to which it leads.

Let $\tau - x$ be the common temperature of the ingredients, as measured from the point of absolute cold;

P their common pressure,

n_1, n_2, n_3, &c. their proportions by weight, in unity of weight of the aggregate;

v_1, v_2, v_3, &c. the respective volumes of unity of weight of the several ingredients;

V the volume of unity of weight of the aggregate;

q_1, q_2, q_3, &c. the respective quantities of actual heat in unity of weight of the several ingredients;

$\mathfrak{k}_1$, $\mathfrak{k}_2$, $\mathfrak{k}_3$, &c. their respective real specific heats;

Q the quantity of heat in unity of weight of the aggregate;

Φ a thermo-dynamic function for the aggregate.

Then these quantities are connected by the following equations:—

$$\Sigma.n=1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50.)$$

$$V=\Sigma.nv. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51.)$$

$$\tau - x = \frac{q_1}{\mathfrak{k}_1} = \frac{q_2}{\mathfrak{k}_2} = \frac{q_3}{\mathfrak{k}_3} = \&c. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52.)$$

$$Q=\Sigma.nq=(\tau - x).\Sigma.n\mathfrak{k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53.)$$

$$\Phi=\int\frac{\Sigma.n(\mathfrak{k}+f'.\tau)}{\tau - x}.d\tau+\int\frac{dP}{d\tau}.dV. \quad . \quad . \quad . \quad . \quad . \quad . \quad (54.)$$

It is evident that all these equations hold whether the proportions of the ingre-

dients n_1, &c. are constant, as in an aggregate of chemically distinct substances, or variable, as in the aggregate of a liquid and its vapour.

Let δH be the heat which disappears in consequence of a small expansion of the aggregate at constant temperature represented by

$$\delta V = \Sigma . \delta u, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55.)$$

δu representing any one of the parts arising from the changes undergone by the different ingredients, of which the whole expansion of the aggregate, δV, is made up. Then

$$\delta H = \Sigma \left\{ (\tau - \varkappa) \frac{dP}{d\tau} . \delta u \right\}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56.)$$

but the pressure P is the same for every ingredient, as well as the temperature; therefore the factor $(\tau - \varkappa) \frac{dP}{d\tau}$ is the same for every ingredient, and consequently for the whole aggregate; that is to say,

$$\delta H = (\tau - \varkappa) \frac{dP}{d\tau} . \delta V = (\tau - \varkappa) \delta \Phi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (57.)$$

This equation shows, that the relation of *temperature* to the mutual transformation of heat and expansive power is the same in an aggregate as in a homogeneous substance.

Consequently, if we define *Isothermal Curves* for an Aggregate to be *Curves of Constant Temperature*, we arrive at the following conclusion:—

Proposition XIV.—Theorem. *Isothermal curves on the diagram of energy of an Aggregate, have the same properties, with reference to the mutual transformation of Heat and Expansive Power, with those on the diagram of energy of a homogeneous substance.*

It is unnecessary to enunciate separately a similar proposition for curves of no transmission; for the demonstration of Proposition I., on which all their properties depend, is evidently applicable to an aggregate constituted in any manner.

Hence it appears, that if the isothermal curves for an aggregate be drawn according to the above definition, all the propositions proved in this paper respecting homogeneous substances become true of the aggregate.

(36.) Proposition XV.—Theorem. *Every Isothermal line for an aggregate of a liquid and its vapour, is a straight line of equal pressure, from the volume corresponding to complete liquefaction to the volume corresponding to complete evaporation.*

This is a fact known by experiment. The Theorem is equivalent to a statement, that the pressure of a liquid and its vapour in contact with each other, is a function of the temperature only.

Corollary.—Theorem. *At any given temperature, the volume of an aggregate of liquid and vapour is arbitrary between and up to the limits of total liquefaction and total evaporation.*

To express this symbolically, let P be the pressure of an aggregate of liquid and

vapour corresponding to the absolute temperature τ; and, unity of weight being the quantity of the aggregate under consideration, let v be the volume corresponding to complete liquefaction, v' that corresponding to complete evaporation, and V the actual volume at any time; let n be the proportion of liquid, and $1-n$ that of vapour, corresponding to the aggregate volume V; then

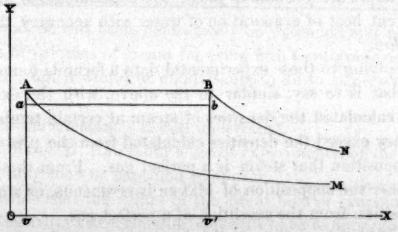
$$V=nv+(1-n)v', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58.)$$

and V may have any value not less than v nor greater than v', while P and τ remain constant; the proportion of liquid, n, being regulated according to the foregoing equation.

(37.) Proposition XVI.—Problem. *The density of a liquid and of its vapour, when in contact at a given temperature, being given, and the isothermal lines of the aggregate; it is required to determine the latent heat of evaporation of unity of weight of the fluid.*

(Solution.) The densities of the liquid and of its vapour, are respectively the reciprocals of the volumes of total liquefaction and total evaporation of unity of weight, above-mentioned. In fig. 20, let the abscissæ Ov, Ov' represent these volumes, and the equal ordinates, vA, $v'B$, the pressure corresponding to the given temperature:

Fig. 20.



so that AB parallel to OX is the isothermal line of the aggregate for that temperature. Suppose two curves of no transmission, AM, BN, to be drawn from A and B respectively, and indefinitely prolonged towards X; then the indefinitely-prolonged area MABN represents the mechanical equivalent of the latent heat sought; and this area is to be computed in the following manner. Draw a second isothermal line ab indefinitely near to AB, at an interval corresponding to the indefinitely-small difference of temperature $d\tau$; then, ultimately,

$$d\tau : \tau-\varkappa :: \text{area } ABba : \text{area } MABN;$$

or, symbolically,

$$L=\text{latent heat of evaporation}=(\tau-\varkappa)\frac{dP}{d\tau}(v'-v). \quad . \quad . \quad . \quad . \quad (59.)$$

This is simply the application of Propositions I. and II. to the aggregate of a liquid and its vapour, *mutatis mutandis*.

(*Remarks.*)—The existence of a necessary relation between the density, pressure, and temperature of a vapour and its liquid in contact, and the latent heat of evaporation, was first shown by CARNÔT. If for $\tau - \varkappa$ in the preceding equation be substituted, according to Professor THOMSON's notation, $\frac{J}{\mu}$, J being "JOULE's equivalent" and μ "CARNÔT's function," the equation is transformed into that deduced by Messrs. CLAUSIUS and THOMSON from the combination of CARNÔT's theory with the law of the mechanical convertibility of heat.

(38.) *Corollary.*—The volume occupied by unity of weight of vapour at saturation may be computed from its latent heat of evaporation by means of the inverse formula,—

$$v' - v = \frac{L}{(\tau - \varkappa)\frac{dP}{d\tau}}; \quad \ldots\ldots\ldots\ldots \quad (60.)$$

the latent heat, L, being of course always stated in units of motive power.

The want of satisfactory experiments on the density of vapours of any kind, has hitherto prevented the use of the direct formula (59.).

It is otherwise, however, with the inverse formula (60.), at all events in the case of steam; for, so far as we are yet able to judge, the experiments of M. REGNAULT have determined the latent heat of evaporation of water with accuracy throughout a long range of temperature.

M. CLAUSIUS, applying to those experimental data a formula founded on the supposition of MAYER (that is to say, similar to the above, with the exception that $\varkappa$ is supposed $=0$), has calculated the densities of steam at certain temperatures, so as to show how much they exceed the densities calculated from the pressures and temperatures, on the supposition that steam is a perfect gas. From these calculations he concludes, that either the supposition of MAYER is erroneous, or steam deviates very much, at high densities, from the condition of a perfect gas.

In the following table, the value of $\varkappa$ is supposed to be 2°·1 Centigrade; and use has been made of the formula for calculating the pressure of steam and other vapours at saturation, first published in the Edinburgh New Philosophical Journal for July 1849, viz.—

$$\log P = \alpha - \frac{\beta}{\tau} - \frac{\gamma}{\tau^3}. \quad \ldots\ldots\ldots\ldots \quad (61.)$$

This table exhibits, side by side, the volume in cubic feet occupied by one pound avoirdupois of steam, at every twentieth Centigrade degree from −20° to +260° (that is, from −4° to +500° Fahrenheit):—first, as extracted from a table for computing the power of steam-engines, in the Transactions of the Royal Society of Edinburgh, vol. xx., which was calculated on the supposition that steam is a perfect gas; and secondly, as computed by equation (60.) from the latent heat of steam as determined by M. REGNAULT. The excess of the former quantity above the latter is also given in each case, with its ratio to the second value of the volume.

For convenience' sake, a column is added containing the pressures of steam corresponding to the temperatures in the table, in pounds per square foot.

Table of Computed Volumes of 1 lb. avoirdupois of Steam.

Temperature.		Volume supposed a Perfect Gas.	Volume computed from Latent Heat.	Difference.	Ratio of difference to lesser value of volume.	Pressure.
Fahrenheit.	Centigrade.					
Deg.	Deg.	Cubic feet.	Cubic feet.	Cubic feet.		lb. per square foot.
− 4	−20	15757	15718	39	0·0025	2·4799
+32	0	3390·4	3377·2	13·2	0·0039	12·431
68	+20	936·81	934·50	2·31	0·0025	48·265
104	40	314·88	313·56	1·32	0·0042	153·34
140	60	123·65	122·63	1·02	0·0083	415·33
176	80	55·05	54·19	0·86	0·0158	988·67
212	100	27·166	26·478	0·688	0·0260	2116·4
248	120	14·596	14·076	0·520	0·0369	4149·3
284	140	8·420	8·004	0·416	0·0502	7557·0
320	160	5·158	4·838	0·320	0·0661	12931
356	180	3·326	3·071	0·255	0·0830	20979
392	200	2·241	2·033	0·208	0·1023	32512
428	220	1·568	1·396	0·172	0·1232	48425
464	240	1·134	0·990	0·144	0·1455	69680
500	260	0·843	0·722	0·121	0·1676	97275
Col. (1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)

The fourth column of this table could easily be extended and filled up, so as to replace the column of volumes of steam for every fifth Centigrade degree in the table previously published; but it would be unadvisable to do so at present, for the following reasons:—

First, the value of the constant $\varkappa$ is still uncertain*.

Secondly, the results of M. Regnault's direct experiments, on the density of steam and other vapours, may soon be expected to appear.

Thirdly, it is possible that the values of the latent heat of evaporation of water, as deduced from M. Regnault's experiments, may still have to undergo some correction; because, according to the theoretical definition of the latent heat of evaporation, the liquid is supposed to be under the pressure of an atmosphere of its own vapour, which atmosphere, as it increases in bulk, performs work of some kind, such as lifting a piston; whereas, in M. Regnault's experiments, the water is pressed by an atmosphere of mingled steam and air, whose united pressure is that corresponding to the temperature of internal ebullition of the water; so that the pressure of the steam alone on the surface of the water, which regulates the superficial evaporation, may be less than the maximum pressure corresponding to the temperature of ebullition; and this steam, moreover, has no mechanical work to perform except to propel itself along the passage leading to the calorimeter, and to agitate the water in the latter vessel. Under these circumstances, it is possible, though by no means certain, that the latent

* It is probable that $\varkappa$ may be found to be inappreciably small; in which case, the numbers in column (4.) will have to be diminished to an extent varying from $\frac{1}{130}$th to $\frac{1}{300}$th of their amount.

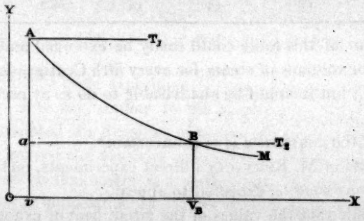
heat of evaporation of water, as deduced from M. REGNAULT's experiments, may be somewhat smaller than that which corresponds to the theoretical definition, especially at high pressures; and a doubt arises as to the precise applicability of the formulæ (59.) and (60.) to those experimental results, which cannot be solved except by direct experiments on the density of steam.

Notwithstanding this doubt, however, the preceding table must be regarded as adding a reason to those already known, for believing that saturated steam of high density deviates considerably from the laws of the perfectly gaseous condition*.

(39.) PROPOSITION XVII.—PROBLEM. *The isothermal lines for a liquid and its vapour, and the apparent specific heat of the liquid at all temperatures being given, and the expansion of the liquid by heat being treated as inappreciably small:—to determine a curve of no transmission for the aggregate, passing through a given point on the ordinate whose distance from the origin approximately represents the volume of the liquid.*

(Solution.) In fig. 21, let O*v* represent the volume of the liquid, assumed to be approximately constant for all temperatures under consideration; let *v*A be an ordinate

Fig. 21.



parallel to OY, and let the heat consumed by the liquid in passing from the temperature corresponding to any point on this ordinate to that corresponding to any other point, be known; let the isothermal lines for the aggregate of liquid and vapour, all of which are straight lines of equal pressure parallel to OX, such as AT_1, aBT_2, be known. Then to draw a curve of no transmission through any point A on the ordinate *v*A, the same process must be followed as in Proposition VIII.

To apply to this case the symbolical representation of Proposition VIII., viz. equation (21.), let τ_1 be the absolute temperature corresponding to the point A (that is, to the isothermal line AT_1); τ_2 that corresponding to any lower isothermal line aBT_2; V_B the volume of the aggregate of liquid and vapour, corresponding to the point B

* Evidence in favour of this opinion is afforded by the experiments recorded by Mr. C. W. SIEMENS (Civil Engineer and Architect's Journal). A remarkable cause, however, of uncertainty in all such experiments, has lately been investigated by Professor MAGNUS (POGGENDORFF's Annalen, 1853, No. 8), viz. a power which solid bodies have of condensing, by attraction on their surfaces, appreciable quantities of gases.

where the curve sought, AM, intersects the latter isothermal line; K_L the apparent specific heat of the liquid;—then making the proper substitutions of the symbols of temperature for those of heat, and observing that the operation

$$\int_{V_A}^{V_B} dV$$

is in this case equivalent to multiplication by $V_B - v$, we have

$$\Delta\Phi = \frac{dP}{d\tau}(V_B - v)(\text{for } \tau = \tau_2) = \int_{\tau_2}^{\tau_1} \frac{K_L}{\tau - \varkappa} d\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad (62.)$$

being an equation between two expressions for the difference between the thermo-dynamic functions Φ for the curve AB, and for that which passes through a.

If the specific heat of the liquid is approximately constant, this equation becomes

$$\Delta\Phi = \frac{dP}{d\tau}(V_B - v)(\text{for } \tau = \tau_2) = K_L \text{ hyp. log } \frac{\tau_1 - \varkappa}{\tau_2 - \varkappa}. \quad . \quad . \quad . \quad . \quad . \quad (63.)$$

(40.) *Corollary.*—PROBLEM. *The same data being given as in the preceding problem, and the expansion of the liquid by heat neglected, a mass of liquid, having been raised from the absolute temperature τ_2 to the absolute temperature τ_1, is supposed to be allowed to evaporate partially, under pressure, without receiving or emitting heat, until its temperature falls again to τ_2, at which temperature it is liquefied under constant pressure by refrigeration: it is required to find the power developed.*

(Solution.) The power developed is represented by the area of the three-sided diagram of energy in fig. 21, ABa; that is to say, by

$$\int_{\tau_2}^{\tau_1} (V - v) \frac{dP}{d\tau} . d\tau = \iint_{\tau_2}^{\tau_1} \frac{K_L}{\tau - \varkappa} d\tau^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (64.)$$

which, if K_L is nearly constant, becomes

$$K_L \int_{\tau_2}^{\tau_1} \text{hyp. log } \frac{\tau_1 - \varkappa}{\tau - \varkappa} . d\tau = K_L \left\{ (\tau_1 - \varkappa) - (\tau_2 - \varkappa) . \left(1 + \text{hyp. log } \frac{\tau_1 - \varkappa}{\tau_2 - \varkappa} \right) \right\}. \quad . \quad (65.)$$

(41.) *Numerical Example.*

Let one pound avoirdupois of water be raised, in the liquid state, from $T_2 = 40°$ Centigrade, to $T_1 = 140°$ Centigrade. Then

$$\tau_1 - \varkappa = T_1 + T_0 = 140° + 272\tfrac{1}{2}° = 412\tfrac{1}{2}° \text{ Centigrade.}$$

$$\tau_2 - \varkappa = T_2 + T_0 = 40° + 272\tfrac{1}{2}° = 312\tfrac{1}{2}° \text{ Centigrade.}$$

The mean apparent specific heat of liquid water between those temperatures is

$K_L = K_W$ (or JOULE's equivalent) $\times 1{\cdot}006 = 1398$ feet per Centigrade degree;

consequently the heat expended is equivalent to 139,800 foot-pounds.

The other numerical data are,—

$\frac{dP}{dt}$ at 40° Centigrade = 8·2075 lbs. per square foot, per Centigrade degree;

v = mean volume of 1 lb. of liquid water = 0·017 cubic foot, nearly.

Let it be required to find, in the first place, V_B, the volume to which the water must be allowed to expand by partial evaporation under pressure, in order that its temperature may fall to 40° Centigrade; and secondly, how much power will be developed in all, after the water has been totally reliquefied by refrigeration at constant pressure, at the temperature of 40°.

First, by the equation (63.),

$$\Delta\Phi = \frac{dP}{dt}(V_B - v) = 1398 \times \text{hyp. log } \frac{412\frac{1}{2}}{312\frac{1}{2}} = 402{\cdot}624;$$

divide by $\frac{dP}{dt} = 8{\cdot}2075$; then $V_B - v = 49{\cdot}055$ cubic feet.

add $v = 0{\cdot}017$

Aggregate volume of water and steam at 40°, $V_B = 49{\cdot}072$ cubic feet.

As the volume of one pound of steam at 40° Centigrade, according to the fourth column of the table in article (38.), is 313·56 cubic feet, it appears from this calculation that somewhat less than one-sixth of the water will evaporate.

Secondly, it appears, from equation (65.), that after the water has been restored to the liquid state by refrigeration at 40° Centigrade, the whole power developed, that is to say, the area ABa, will be

$$1398 \text{ foot-pounds} \times \left\{412{\cdot}5 - 312{\cdot}5\left(1 + \text{hyp. log } \frac{412{\cdot}5}{312{\cdot}5}\right)\right\}$$

$$= 1398 \text{ ft. lb.} \times 10° \text{ Centigrade} = 13{,}980 \text{ ft. lb.},$$

or one-tenth of the equivalent of the heat expended. The other nine-tenths constitute the heat abstracted during the reliquefaction at 40° Centigrade.

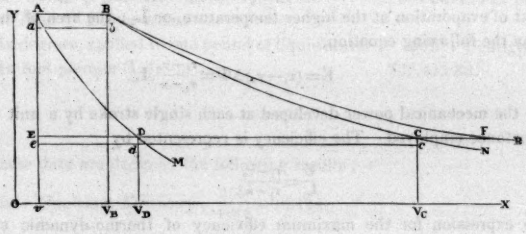
This calculation further shows, that in order that one pound of water and steam at 40° C. may be raised to 140° C. solely by compressing it into the liquid state, it must occupy at the commencement of the operation the volume $V_B = 49{\cdot}072$ cubic feet; and that the power expended in the compression will be as follows:—

	Foot-pounds.
Area of the curvilinear triangle ABa, fig. 21, as already calculated	13,980
Area of the rectangle $a\mathrm{B}V_B v = P_2(V_B - v) =$	7,522
Total	21,502

(42.) Proposition XVIII.—Problem. *Having the same data as in the last proposition, it is required to draw a curve of no transmission through any point on the diagram of energy for the aggregate of a liquid and its vapour.*

(Solution.) In fig. 22, through the given point B draw the straight isothermal line AB corresponding to the absolute temperature τ_1, and cutting the ordinate corresponding to the volume of total liquefaction in A. Through A, according to the last proposition, draw the curve of no transmission, ADM. Let EDC be any other isothermal line, corresponding to the absolute temperature τ_2, and cutting the curve AM in D. Draw isothermal lines *ab*, *edc* at indefinitely small distances from AB,

Fig. 22.



EDC respectively, corresponding to the same indefinitely small difference of temperature $\delta\tau$. Draw the ordinates $V_D dD$, $V_B bB$; then draw the ordinate $V_C cC$ at such a distance from $V_D dD$, that the indefinitely small rectangles $DCcd$, $ABba$ shall be equal. Then as the difference $\delta\tau$ is indefinitely diminished, C approximates indefinitely to a point on the required curve of no transmission, BN.

This is Proposition III. applied to aggregates, *mutatis mutandis*.

The symbolical representation of this proposition is as follows:—let P_1 and P_2 be the pressures of the aggregate of liquid and vapour corresponding respectively to the temperatures τ_1 and τ_2; then the following expressions for the difference between the thermo-dynamic functions Φ of the curves AM, BN are equal,

$$\Delta\Phi = \frac{dP_2}{d\tau}(V_C - V_D) = \frac{dP_1}{d\tau}(V_B - v). \quad . \quad . \quad . \quad . \quad . \quad . \quad (66.)$$

(43.) *Corollary.* (*Absolute Maximum Efficiency of Vapour-Engines.*)

If the volume V_B be that corresponding to complete evaporation at the temperature τ_1, that is to say, if

$$V_B = v',$$

then the curve BCN will represent the mode of expansion under pressure, of vapour of saturation in working an engine, and will be defined by the equation

$$V_C - V_D = \frac{\frac{dP_1}{d\tau}(v' - v)}{\frac{dP_2}{d\tau}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67.)$$

If in this equation be substituted the value of $v'-v$ in terms of the latent heat of evaporation at the higher temperature, given by equation (60.), it becomes

$$V_C - V_D = \frac{L_1}{(\tau_1 - x)\frac{dP_2}{d\tau}}. \quad \ldots\ldots\ldots \quad (68.)$$

In this case the diagram ABCD, fig. 22, is evidently that of a vapour-engine working with the absolute maximum of efficiency between the absolute temperatures τ_1 and τ_2. The heat expended at each single stroke, per unit of weight of fluid, is the latent heat of evaporation at the higher temperature, or L_1; the area of the diagram is given by the following equation,

$$E = (\tau_1 - \tau_2)\Delta\Phi = \frac{\tau_1 - \tau_2}{\tau_1 - x} . L_1. \quad \ldots\ldots\ldots \quad (69.)$$

This is the mechanical power developed at each single stroke by a unit of weight of the substance employed. The efficiency is represented by

$$\frac{E}{L_1} = \frac{\tau_1 - \tau_2}{\tau_1 - x}, \quad \ldots\ldots\ldots\ldots \quad (70.)$$

being the expression for the maximum efficiency of thermo-dynamic engines in general.

The conditions of obtaining this efficiency are the following :—

First; that the elevation of temperature from τ_2 to τ_1, during the operation represented by the curve DA on the diagram, shall be produced entirely by compression. The volume at which this heating by compression must commence is given, according to Proposition XVII., by the following equation :—

$$V_D = v + \frac{1}{\frac{dP_2}{d\tau}} . K_L \text{ hyp. log } \frac{\tau_1 - x}{\tau_2 - x}. \quad \ldots\ldots \quad (71.)$$

Secondly; that the expansive working of the vapour shall be carried on until the temperature falls, by expansion alone, to its lower limit; that is to say, until the volume reaches the following value, obtained by adding together equations (68.) and (71.) :—

$$V_C = v + \frac{1}{\frac{dP_2}{d\tau}} . \left\{ K_L \text{ hyp. log } \frac{\tau_1 - x}{\tau_2 - x} + \frac{L_1}{\tau_1 - x} \right\}. \quad \ldots\ldots \quad (72.)$$

(44.) *Numerical example.*

To exemplify this numerically, let the same data be employed as in article (41.), the substance working being one pound avoirdupois of water. These data, with some additional data deduced from them, are given in the following table :—

	At upper limit of Actual Heat.	At lower limit of Actual Heat.
Temperature in Centigrade Degrees:—		
Above melting ice (T)	140°	40°
Above zero of gaseous tension (τ) . . .	414·6	314·6
Above absolute cold ($\tau - x$)	412·5	312·5
Pressure in pounds per square foot (P)	7557	153·34
„ „ per square inch	52·5	1·065

Initial Volume of saturated steam, $V_B = v'_1 = \ldots$ 8·004 cubic feet per pound.

Latent Heat of Evaporation:—

In degrees, applied to one pound of liquid water 509°·1 Centigrade.

In foot-pounds (L_1) . . . . . 707,445·36.

From these data are deduced the following results:—

Absolute Maximum Efficiency; $\frac{100}{412·5} = 0·2424$.

Duty of one pound of water; being the area of the diagram ABCD . . . . . 171,484·75 ft. lb.

Volume at which the compression must commence; calculated as in art. (41.) . . $V_D = 49·1$ cubic feet per pound.

Volume to which the Expansion must be carried; calculated by equation (72.) . . $V_C = 258·1$ cubic feet per pound.

Ratio of Expansion . . . . . $= \frac{V_C}{V_B} = \frac{258·1}{8·004} = 32·25$.

(45.) *Liquefaction of Vapour by Expansion under Pressure.*

In fig. 22, let the abscissæ of the curve BFR indicate the volumes corresponding to complete evaporation at the pressures denoted by its ordinates. For most known fluids, a curve of no transmission BCN, drawn from any point B of the curve of complete evaporation in the direction of X, falls within that curve; so that by expansion of saturated vapour under pressure, a portion in most cases will be liquefied.

To ascertain whether this will take place in any particular case, and to what extent, equation (60.), which gives the volume of unity of weight of saturated vapour at the temperature τ_2, is to be compared with equation (72.), which gives the volume at the same temperature of unity of weight of an aggregate of liquid and vapour, which has expanded under pressure from a state of complete evaporation at the temperature τ_1. The difference between the volumes given by these equations is as follows (neglecting, as usual, the expansibility in the liquid state):—

$$v'_2 - V_C = \frac{1}{\frac{dP_2}{d\tau}} \cdot \left\{ \frac{L_2}{\tau_2 - x} - \frac{L_1}{\tau_1 - x} - K_L \cdot \text{hyp. log} \frac{\tau_1 - x}{\tau_2 - x} \right\} \quad \ldots \quad (73.)$$

That this quantity is almost always positive appears from the following considerations. The latent heat of evaporation L is in general capable of being represented approximately by an expression of this form:

$$L = a - b(\tau - \varkappa). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (74.)$$

(For water, $a = 796°$ Centigr. $\times K_w = 1{,}106{,}122$ ft. lb.; $b = 0{\cdot}695 \times K_w = 965{\cdot}772$ ft. lb. per Centigrade degree.)

Hence the second factor in equation (73.) is nearly equal to

$$\frac{a(\tau_1 - \tau_2)}{(\tau_1 - \varkappa).(\tau_2 - \varkappa)} - K_L . \text{hyp. log} \frac{\tau_1 - \varkappa}{\tau_2 - \varkappa}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (75.)$$

Now

$$\text{hyp. log} \frac{\tau_1 - \varkappa}{\tau_2 - \varkappa} < \frac{\tau_1 - \tau_2}{\tau_2 - \varkappa}.$$

Therefore the expression (75.) is positive so long as

$$\frac{a}{\tau_1 - \varkappa} \text{ exceeds } K_L, \text{ the specific heat of the liquid.} \quad . \quad . \quad . \quad (75\text{ A.})$$

For Water, this condition is fulfilled for all temperatures lower than $523\frac{1}{2}°$ Centigrade (at which $\tau_1 - \varkappa = 796°$ Centigrade); and there is reason to believe that it is fulfilled also for other fluids at those temperatures at which their vapours can be used for any practical purpose.

To determine the proportion of the fluid which is liquefied by a given expansion under pressure, we have the following formula, deduced from equation (58.):—

$$n = \frac{v'_2 - V_0}{v'_2 - v}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (76.)$$

As a numerical example, we may take the case of art. (44.), where saturated steam at 140° Centigrade is supposed to be expanded under pressure until its temperature falls to 40° Centigrade. The volume of one pound of water and steam at the end of the expansion has already been found to be

$$V_0 = 258{\cdot}1 \text{ cubic feet.}$$

While, according to the table in article (38.), the volume of a pound of steam at that temperature is

$$v'_2 = 313{\cdot}56 \text{ cubic feet.}$$

Consequently the fraction liquefied by the expansion is

$$n = \frac{313{\cdot}56 - 258{\cdot}1}{313{\cdot}56 - 0{\cdot}016} = \frac{55{\cdot}46}{313{\cdot}544} = 0{\cdot}177.$$

This conclusion was arrived at contemporaneously and independently, by M. Clausius and myself, about four years since. Its accuracy was subsequently called in question, chiefly on the ground of experiments, which show that steam, after being expanded by being "wire-drawn," that is to say, by being allowed to escape through a narrow orifice, is super-heated, or at a higher temperature than that of liquefaction at the reduced pressure. Soon afterwards, however, Professor William Thomson

proved that those experiments are not relevant against the conclusion in question, by showing the difference between the *free expansion* of an elastic fluid, in which all the power due to the expansion is expended in agitating the particles of the fluid, and is reconverted into heat, and the expansion of the same fluid *under a pressure equal to its own elasticity*, when the power developed is all communicated to external bodies, such, for example, as the piston of an engine.

The free expansion of a vapour will be considered in the sequel.

(46.) *Efficiency of a Vapour-Engine without heating by compression.*

The numerical example of article (44.) sufficiently illustrates the fact, that the strict fulfilment of the condition specified in article (43.), as necessary to the attainment of the absolute maximum of efficiency of a vapour-engine, is impossible in practice.

Let us consider, in the first place, the effect of dispensing with the process DA, during which the fluid is supposed to have its high temperature restored solely by compression.

The effect of this modification is evidently, to add to the heat expended, that which is necessary to elevate the temperature of the liquid from τ_2 to τ_1, and to add to the power developed an amount represented by the area ADE, fig. 22.

To express this symbolically, we have—

The Latent Heat of Evaporation at τ_1, as before . . L_1

The additional heat expended (K_L being the *mean specific heat* of the liquid between τ_1 and τ_2) . . . $K_L(\tau_1-\tau_2)$

Total heat expended . . $L_1+K_L(\tau_1-\tau_2)$. (77.)

Then for the power developed, we have

the area ABCD, as in article (43.), $=\frac{\tau_1-\tau_2}{\tau_1-x}.L_1$,

the area ADE, as in Article (40), equation (65.),

$$=K_L\left\{(\tau_1-x)-(\tau_2-x)\left(1+\text{hyp. log}\frac{\tau_1-x}{\tau_2-x}\right)\right\}$$

the sum of which quantities is the total power developed. . . . . (78.)

The efficiency may be expressed in the following form :—

$$\frac{\text{Power developed}}{\text{Heat expended}}=\frac{\tau_1-\tau_2}{\tau_1-x}-\frac{K_L(\tau_2-x)\left\{\text{hyp. log}\frac{\tau_1-x}{\tau_2-x}-\frac{\tau_1-\tau_2}{\tau_1-x}\right\}}{L_1+K_L(\tau_1-\tau_2)}, \quad . \quad . \quad . \quad . \quad (79.)$$

an equation which shows at once how far the efficiency falls short of the absolute maximum.

For a numerical example, the same data may be taken as in articles (41.) and (44.). Then the heat expended, per pound of steam, is thus made up :—

	Foot-pounds.
Latent Heat of Evaporation, as in art. (44.)	707,445·36
Heat required to raise the water 100° C., as in article (41.) .	139,800·00
Total heat expended, per lb. of water . . .	847,245·36

The power developed consists of,—

	Foot-pounds.
The area ABCD, as in article (44.)	171,484·75
The area ADE, as in article (41.)	13,980·00
Total power developed, per lb. of water . .	185,464·75

Efficiency, $\frac{185,484·75}{847,245·36}$	= 0·2189
Absolute maximum efficiency, as in art. (44.)	0·2424
Loss of efficiency by omitting the heating by compression	0·0235

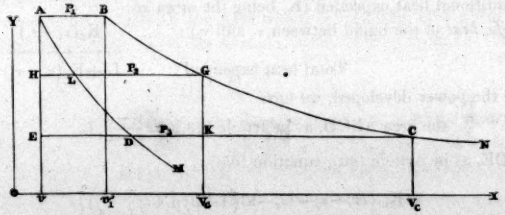
or about one-tenth part of the absolute maximum.

(47.) *Efficiency of a Vapour-Engine with incomplete expansion.*

It is in general impossible in practice to continue the expansion of the vapour down to the temperature of final liquefaction; and from this cause a further loss of efficiency is incurred.

Let it be supposed, for example, that while the pressure of evaporation P_1 corresponds to the line AB in fig. 23, and the pressure of liquefaction, P_2, to the line EDC, the

Fig. 23.



pressure at which the expansion terminates, P_3, corresponds to an intermediate line HLG. Let vA, v'_1B, as before, be the ordinates corresponding to complete liquefaction, and to complete evaporation, at the pressure P_1.

Draw, as before, the curves of no transmission AM, BN, cutting HLG in L and G, and EDC in D and C; draw also the ordinate V_0KG, cutting EDC in K.

Then the expansion terminates at the volume V_0, and ABGKE is the indicator-diagram of the engine.

To find the power represented by this diagram, the area ALH is to be found as in article (40.), the area ABGL as in article (43.), and the rectangle HGKE by multiplying its breadth $V_0 - v$ (found as in article (43.)) by its height HE, which is the excess of the pressure at the end of the expansion, P_3, above the pressure of final liquefaction, P_2.

Hence we have the following formula for the indicated power developed, per unit of weight of fluid evaporated.

$$\left.\begin{aligned} E=\text{area ABGKE}=K_L\left\{(\tau_1-\tau)-(\tau_2-\tau)\left(1+\text{hyp. log}\,\frac{\tau_1-\tau}{\tau_2-\tau}\right)\right\}+L_1\cdot\frac{\tau_1-\tau_2}{\tau_1-\tau} \\ +(P_2-P_3)\frac{1}{\frac{dP_2}{d\tau}}\left\{\frac{L_1}{\tau_1-\tau}+K_L\,\text{hyp. log}\,\frac{\tau_1-\tau}{\tau_2-\tau}\right\}. \quad . \quad . \quad . \quad . \end{aligned}\right\} \quad (80.)$$

The heat expended is of course $L_1+K_L(\tau_1-\tau_2)$.

To illustrate this numerically, let the fluid be water; let the temperature of evaporation be 140° Centigrade, and that of liquefaction 40°, as in the previous examples; and let the expansion terminate when the pressure has fallen to 100° Centigrade.

The numerical data in this case are the following:—

	1. During the evaporation.	2. At the end of the expansion.	3. During the final liquefaction.
Temperature in Centigrade degrees:—			
Above melting ice	140°	100°	40°
Above zero of gaseous tension, τ= .	414·6	374·6	314·6
Above absolute cold, $\tau-\tau$	412·5	372·5	312·5
Pressure, in lb. per square foot, P= . .	7557	2116·4	153·34
Pressure, in lb. per square inch	52·5	14·7	1·065
$\frac{dP}{d\tau}$ in lb. per sq. foot per Centigr. deg. . .	214·16	75·617	8·2075
Initial Volume of steam in cubic feet per lb.	8·004		
Latent Heat of Evaporation, L_1, in foot-pounds per pound of steam . . .	707,445·36		
Total heat expended, in foot-pounds per lb. of steam	847,245·36		
Mean specific heat of liquid water—			
Between 40° and 140° C.	1398 feet of fall.		
Between 100° and 140° C.	1409 feet of fall.		

Applying equation (80.) to these data, we obtain the following results:—

	Foot-pounds.
Area ALH	2,818
Area ABGL	68,601
Area HGKE = $(P_2-P_3).(V_G-v)$ = 1963 lbs. per square foot × 24·58 cubic feet	=48,250
Total power developed by 1 lb. of water evaporated	119,669

	Foot-pounds.
Efficiency $=\frac{119,669}{847,245}$	$=0{\cdot}1413$
Efficiency computed in the last article	0·2189
Difference=loss of Efficiency by incomplete expansion .	0·0776

Ratio of Expansion $\frac{V_G}{v}=\frac{24{\cdot}60}{8{\cdot}004}=3{\cdot}07$ nearly.

If the power of the same engine be now computed by the tables and formulæ published in the 20th volume of the Transactions of the Royal Society of Edinburgh, which were calculated on the supposition that steam is sensibly a perfect gas, the following results are obtained:—

Ratio of expansion, $\frac{24{\cdot}60}{8{\cdot}4204}=2{\cdot}921=s$ in tables.

	Foot-pounds.
"Action at full pressure" (P_1V_1 in tables)	63,633
"Coefficient of Gross Action" (Z in tables) for the expansion 2·921	1·98
Gross Action (P_1V_1Z)	125,993 ft. lb.
Deduct for back-pressure of liquefaction $P_2V_G=153{\cdot}34\times24{\cdot}6$.	3,772 ft. lb.
Power developed per pound of steam . .	122,221 ft. lb.

This result is too large by about one forty-seventh part; a difference to be ascribed chiefly to the error of treating steam as a perfect gas. This difference, however, is not of material consequence in computing theoretically the power of a steam-engine, being less than the amount of error usually to be expected in such calculations.

(48.) My object in entering thus minutely into the theory of the efficiency of vapour-engines is, not so much to provide new formulæ for practical use, as to illustrate the details of the mechanical action of heat under varied and complicated circumstances, and to show with precision the nature and influence of the circumstances which prevent the production, by steam-engines, of the absolute maximum of efficiency corresponding to the temperatures between which they work.

To illustrate the results of these calculations with respect to the consumption of coal, let it be assumed, as in article (33.), that each pound of coal consumed in the furnace communicates to the water, or air, or other elastic substance which performs the work, an amount of heat equivalent to 6,000,000 foot-pounds, which corresponds to a power of evaporating, in round numbers, about seven times its weight of water. Then the following calculation shows the theoretical indicated duty of one pound of such coal, when the limits of working temperature are 140° and 40° Centigrade, at the absolute maximum of theoretical efficiency, and at the reduced efficiency computed in the preceding article, on the supposition that the expansive working ceases at the atmospheric pressure.

	Efficiency.		Effect per pound of coal in foot-pounds.	
Absolute Theoretical Maximum, being the same for every perfect Thermo-dynamic Engine working between the same limits of temperature, $\frac{140°-40°}{140°+272\frac{1}{2}°}$		0·2424		1,454,400
Deductions:—				
For raising the temperature of the feed-water from 40° to 140° Centigrade	0·0235		141,000	
For stopping the expansive working at 3·07 times the initial volume instead of 32 times	0·0776		465,600	
		0·1011		606,600
Reduced Efficiency and Effect		0·1413		847,800

The last of these quantities corresponds to a consumption of about 2·34 lbs. of coal per indicated horse-power per hour.

The conditions of the preceding investigation are very nearly fulfilled in steam-engines with valves and steam-passages so large, and a velocity of piston so moderate, that the pressure in the cylinder during the admission of the steam is nearly the same with that in the boiler.

In many steam-engines, however, the steam is more or less "wire-drawn"; that is to say, it has to rush through the passages with a velocity, to produce which there is required a considerable excess of pressure in the boiler above that in the cylinder. The power developed during the expansion of the steam from the pressure in the boiler to that in the cylinder is not altogether lost; for, as already stated in article (45.), it is expended in agitating the particles of the steam, and is ultimately converted into heat by friction, so that the steam begins its action on the piston in a super-heated state; and both its initial pressure and its expansive action are greater than those of steam of saturation of the same density. The numerical relations of the temperature, pressure, and density of super-heated steam are not yet known with sufficient precision to constitute the groundwork of a system of exact formulæ representing its action. Some general theorems, however, will be proved in the sequel, respecting super-heated vapours, which may be found useful when the necessary experimental data have been obtained.

Calculation and experiment concur to prove, that in Cornish single-acting engines, the initial pressure of the steam in the cylinders is very much less than the maximum pressure in the boilers; generally, indeed, less than one-half*. It is doubtful, however, whether this arises altogether from wire-drawing in the steam-passages and valves; for when it is considered, that in such engines, even at their greatest speed, the steam-valve remains shut during nearly the whole of each stroke, being opened during a small portion of the stroke only, it may be regarded as probable, that the

* See Mr. Pole's work on the Cornish Engine, and article 36 of a paper on the Mechanical Action of Heat, Trans. Roy. Soc. Edinb. vol. xx.

sudden opening of this valve causes a temporary reduction of temperature and pressure in the boiler itself.

(49.) *Composite Vapour-Engines.*

The Steam-and-Ether Engine of M. DU TREMBLEY is an example of what may be called a *Composite Vapour-Engine*, in which two fluids are employed, a less and a more volatile; the heat given out during the liquefaction of the less volatile fluid serving to evaporate the more volatile fluid, which works an auxiliary engine, and is liquefied in its turn by refrigeration.

Let the efficiency of the engine worked by the less volatile fluid be expressed in the form

$$1-\frac{1}{n};$$

so that $\frac{1}{n}$ is the fraction of the whole heat expended which is given out to the more volatile fluid. Let the efficiency of the engine worked by the more volatile fluid be

$$1-\frac{1}{n'};$$

then the efficiency of the combined engines will be

$$1-\frac{1}{nn'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (81.)$$

If both the engines are perfect thermo-dynamic engines, let τ_1 be the absolute temperature at which the first fluid is evaporated; τ_2 that at which it is condensed, and the second fluid evaporated; and τ_3 that at which the second fluid is condensed; then,

$$1-\frac{1}{n}=1-\frac{\tau_2-\kappa}{\tau_1-\kappa}; \quad 1-\frac{1}{n'}=1-\frac{\tau_3-\kappa}{\tau_2-\kappa}; \quad 1-\frac{1}{nn'}=1-\frac{\tau_3-\kappa}{\tau_1-\kappa}; \quad . \quad . \quad (81\text{A.})$$

being equal to the theoretical maximum efficiency of a simple thermo-dynamic engine working between the limits of temperature τ_1 and τ_3.

Composite Vapour-Engines, therefore, have the same theoretical maximum efficiency with simple vapour-engines, and other engines moved by heat, working between the same temperatures; but they may, nevertheless, enable the same efficiency to be obtained with smaller engines.

(50.) *Curves of Free Expansion for Nascent Vapour.*

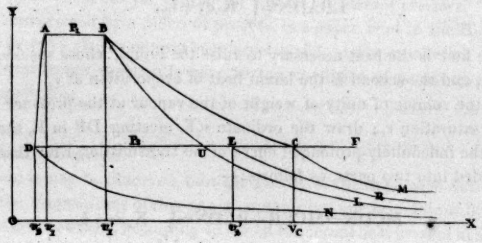
By *Nascent Vapour* is to be understood, that which is in the act of rising from a mass of liquid. If this vapour be at once conducted to a condenser, without performing any work, and there liquefied at a temperature lower than that at which it was evaporated, its expansion, from the pressure of evaporation down to the pressure of liquefaction, will take place according to a law defined by a curve analogous in some respects, but not in all, to the curve of free expansion for a homogeneous substance referred to in Proposition VI. To determine theoretically the form of this curve, it is necessary to know the properties of the isothermal curves and curves of no transmission for the fluid in question in the gaseous state, when above the tem-

perature of saturation for its pressure. Having these data, we can solve numerically the following problem :—

PROPOSITION XIX.—PROBLEM. *To draw the curve of Free Expansion for vapour nascent under a given pressure.*

(Solution.) In fig. 24, let AB, parallel to OX, be the isothermal line of an aggregate of liquid and vapour at the pressure of evaporation P_1 corresponding to the temperature τ_1: let Av_1, Bv'_1 be ordinates parallel to OY; so that v_1 is the volume of

Fig. 24.



unity of weight of the liquid at this temperature, and v'_1 that of unity of weight of the vapour, at saturation. Let DF be a line drawn parallel to OX, at a distance representing any lower pressure P_2 corresponding to the temperature τ_2. It is required to find the point where the curve of free expansion drawn from B intersects DF.

Let v_2 be the volume of unity of weight of the liquid at the lower pressure and temperature, v_2D an ordinate parallel to OY, and DA a curve representing the law of expansion of the liquid as the pressure and temperature increase. Draw the curves of no transmission DN, BL indefinitely prolonged towards X; ascertain the indefinitely-prolonged area LBADN; draw a curve of no transmission MC, cutting DF in C, such that the indefinitely-prolonged area MCDN shall be equal to the indefinitely-prolonged area LBADN; then will C be the point required, where the curve of free expansion BC intersects the line DF.

(Demonstration.) Unity of weight of the fluid being raised in the liquid state from the temperature τ_2 and corresponding pressure P_2 to the temperature τ_1 and corresponding pressure P_1; then evaporated completely at the latter pressure and temperature; then expanded without performing work, until it falls to the original pressure P_2; then cooled at this pressure till it returns to the original temperature τ_2, at which it is finally liquefied;—the area ABCD represents the expansive power developed during this cycle of operations, which, as no work is performed, must be wholly expended in agitating the fluid, and reproducing, by friction, the heat consumed by the free expansion represented by the curve BC; which heat is measured by the indefinitely-prolonged area MCBL; which area is therefore equal to the area ABCD.

Subtracting from each of these equal areas the common area BUC, and adding to each of the equal remainders the indefinitely prolonged area LUDN, we form the areas MCDN, LBADN; which are consequently equal. Q.E.D.

(51.) *Of the Total Heat of Evaporation.*

The symbolical expression of the preceding proposition is formed in the following manner. The area LBADN represents the *total heat of evaporation, at* the temperature τ_1, *from* the temperature τ_2, and is composed of two parts, as follows:—

$$\text{LBADN}=\int_{\tau_2}^{\tau_1} K_L d\tau + L_1, \quad \ldots\ldots\ldots \quad (82.)$$

of which the first is the heat necessary to raise the liquid, whose specific heat is K_L, from τ_2 to τ_1, and the second is the latent heat of evaporation at τ_1.

Let v'_2 be the volume of unity of weight of the vapour at the pressure P_2 and temperature of saturation τ_2; draw the ordinate v'_2E, meeting DF in E, through which point draw the indefinitely-prolonged curve of no transmission ER: then is the area MCDN divided into two parts, as follows:—

$$\text{MCDN}=\text{MCER}+\text{REDN}=\int_{\tau_2}^{\tau_C} K_P d\tau + L_2, \quad \ldots\ldots \quad (83.)$$

in which equation τ_C denotes the temperature corresponding to the point C on the curve of free expansion, and K_P the specific heat of the vapour, at the constant pressure P_2 when above the temperature of saturation; so that the first term represents the heat abstracted in lowering the temperature of the vapour from τ_C to the temperature of saturation τ_2, at the constant pressure P_2; and the second term, the latent heat of evaporation at τ_2, abstracted during the liquefaction.

By equating the formulæ (82.) and (83.), the following equation is obtained:—

$$\int_{\tau_2}^{\tau_1} K_L d\tau + L_1 - L_2 = \int_{\tau_2}^{\tau_C} K_P d\tau, \quad \ldots\ldots\ldots \quad (84.)$$

which is the symbolical solution of Proposition XIX., and shows a relation between the total heat of evaporation of a fluid, the free expansion of its vapour, and the specific heat of that vapour at constant pressure.

(52.) *Approximate Law for a Vapour which is a perfect gas.*

If the vapour of the fluid in question be a perfect gas, and of very great volume as compared with the fluid in the liquid state, the curve BC will be nearly a hyperbola, and will nearly coincide with the isothermal curve of the higher temperature τ_1, to which, consequently, τ_C will be nearly equal; and the following equation will be approximately true:

$$\int_{\tau_2}^{\tau_1} K_L d\tau + L_1 - L_2 = \int_{\tau_2}^{\tau_1} K_P d\tau, \quad \ldots\ldots\ldots \quad (85.)$$

which, when the difference between the higher and lower temperatures diminishes indefinitely, is reduced to the following :—

$$K_L + \frac{dL}{d\tau} = K_P, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (86.)$$

that is to say :—

COROLLARY.—THEOREM. *When a vapour is a Perfect Gas, and very bulky as compared with its liquid, the rate of increase of the total heat of evaporation with temperature is nearly equal to the specific heat of the vapour at constant pressure.*

This was demonstrated by a different process, in a paper read to the Royal Society of Edinburgh in 1850. It has not yet been ascertained, however, whether any vapour at saturation approaches sufficiently near to the condition of perfect gas to render the theorem applicable.

(53.) *Concluding Remarks.*

In conclusion, it may be observed, that the Theory of the Expansive Action of Heat embodied in the propositions of this paper contains but one principle of hypothetical origin; viz. Proposition XII., according to which the actual heat present in a substance is simply proportional to its temperature, measured from a certain point of absolute cold, and multiplied by a specific constant; and that although existing experimental data may not be adequate to verify this principle precisely, they are still sufficient to prove, that it is near enough to the truth for all purposes connected with Thermo-dynamic Engines, and to afford a strong probability that it is an exact physical law.

PHILOSOPHICAL TRANSACTIONS.

VII. The Bakerian Lecture.—*On Osmotic Force.*

By Thomas Graham, *F.R.S.* &c.

Received June 15,—Read June 15, 1854.

THE expression "Osmotic Force" (from ὠσμὸς, *impulsio*) has reference to the endosmose and exosmose of Dutrochet.

We may succeed in covering a solution of salt occupying the lower part of a glass jar by a stratum of pure water without much intermixture of the two liquids. A force, however, is thereby brought into action which carries up the salt in a gradual manner, dispersing it and ultimately producing a uniform mixture of the salt with the whole volume of water. The molecules of salt have the liquid condition when in solution as well as those of water itself, and we have in the experiment the contact of two different liquids, which must of necessity diffuse through each other, the molecules of a liquid being self-repellent, or subject to a force the same in kind but less in degree as that which gives to gases their elasticity and diffusibility.

The force of liquid diffusibility will still act if we interpose between the two liquids a porous sheet of animal membrane or of unglazed earthenware; for the pores of such a septum are occupied by water, and we continue to have an uninterrupted liquid communication between the water on one side of the septum and the saline solution on the other side.

To impel by pressure any liquid through the pores of such a septum may be extremely difficult, from the interference of frictional resistance and the attraction of capillarity. But these last forces act on masses and not on molecules, and the ultimate particles of water and salt which alone diffuse, appear really to permeate the channels of the porous septum with little or no impediment. A comparative experiment on diffusion, with and without septa, is easily made by means of a wide-mouthed phial, which is filled completely with the saline solution and then immersed in water, in one experiment with the mouth of the phial open, and in the other experiment with the mouth covered by membrane. In a fixed time, such as seven days, a certain quan-

tity of salt leaves the phial by diffusion. This quantity was reduced to one-half when the strong and thiek membrane of the ox-gullet was used to cover the mouth of the phial; and it was not affected in a sensible degree by passing through a thinner membrane, consisting of ox-bladder with the outer muscular coat removed. In the last experiment the actual diffusates were 0·631 gramme common salt in the absence of the membrane, and 0·636 gramme common salt with the membrane interposed, which may be considered as the same quantity. The diffusion of a salt appears to take place, therefore, without difficulty or loss through the substance of a thin membrane, although the mechanical flow of a liquid may be nearly stopped by such an obstacle.

It is well to bear in mind the last fact in the consideration of what is seen in an endosmotic experiment. An open glass tube, with one end expanded into a bell form and covered by tight membrane, forms a vessel which may be filled with a saline solution and immersed in a jar of pure water. The volume of liquid in this osmometer soon begins to increase and is observed to rise in the tube, while the simultaneous appearance of salt in the water of the jar may easily be verified. M. Dutrochet described the result as the movement of two unequal streams through the membrane in opposite directions, the smaller stream being that of the saline solution flowing outwards, and the larger that of pure water flowing inwards. The double current has been always puzzling, but the expression of the fact becomes more conceivable when we say (as we may do truly) that the molecules of the salt travel outwards by diffusion through the porous membrane. It is not the whole saline liquid which moves outwards, but merely the molecules of salt, their water of solution being passive. The inward current of water, on the other hand, appears to be a true sensible stream or a current carrying masses. The passage outwards of the salt is inevitable, and being fully accounted for by diffusibility, requires no further explanation. It is the water current which requires consideration, and for which a cause must be found. This flow of water through the membrane I shall speak of as osmose, and the unknown power producing it as the osmotic force. It is a force of great intensity, capable of supporting a column of water many feet in height, as shown in Dutrochet's well-known experiments, and to which naturalists are generally disposed to ascribe a wide sphere of action, both in the vegetable and animal kingdoms.

Cannot liquid diffusion itself, it may first be asked, contribute to produce osmose? Diffusion is always a double phenomenon, and while molecules of salt pass in one direction through the membrane, molecules of water no doubt pass by diffusion in the opposite direction at the same time, and replace the saline molecules in the osmometer. Water also is probably a liquid of a high degree of diffusibility, at least it appears to diffuse four times more rapidly than alcohol, and four or six times more rapidly therefore than the less diffusive salts. A possible consequence of such inequality of diffusion is, that while one grain of a certain salt diffuses out of the osmometer, four or six grains of water may diffuse into the osmometer. Liquid diffusion, I believe, generally tends to increase the volume of liquid in the osmometer, and a

portion, if not the whole, of the small osmose of chloride of sodium, sulphate of magnesia, alcohol, sugar, and many other organic substances may be due to the relatively low diffusibility of such liquefied bodies compared with the diffusibility of water. But many substances, it will immediately appear, are replaced in experiments of endosmose, not by four or six, but by several hundred times their volume of water, and manifestly some other force besides diffusion is at work in the osmometer.

An explanation of osmose has been looked for in capillarity by Poisson, Magnus, and by Dutrochet himself. Combining diffusion with this idea, we might imagine that the pure water which first occupies the pores of the septum, suffers a sudden and great loss of its capillarity-force when the salt of the osmometer enters the pores by diffusion and mixes with the water they contain. Experiments published by Dutrochet give a capillary ascension to pure water of 12 millimeters, and to a solution of common salt, of density 1·12, 6·14 millimeters, or only one-half of the former ascension. If a porous septum, occupied by such a saline solution, had the same solution in contact with one surface and pure water in contact with the other surface (the actual condition of the septum in an osmotic experiment), the pure water should enter the pores from its high capillary attraction, and, like a solid piston, force out the saline solution from them: the saline solution so displaced would go to swell the liquid within the osmometer. When the pure water, now again occupying the pores, came in time to acquire salt by diffusion, the displacement would be repeated, and a continuous osmose or flow of water inwards be in fact established.

This explanation is attended with certain physical difficulties, but it is unnecessary to discuss these, as the experimental basis of the hypothesis is unsound. The great inequality of capillarity assumed among aqueous fluids does not exist. Many saline solutions which give rise to the highest osmose are, I find, undistinguishable in capillarity from pure water itself. To obtain constant results with saline solutions, the capillary tube must be retained for some minutes in the saline solution at a boiling temperature, and afterwards be cooled without removal from the liquid, otherwise the indications are singularly irregular and most fallacious.

The near equality in capillarity of solutions of the most different composition is very apparent in my observations, which are placed together in the following series of capillary ascensions:—

Capillary ascension of several liquids in the same glass tube.

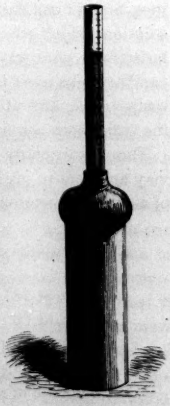
	Millimeters.
Water, at 58° Fahr.	17·75
Water, at 66°	17·55
Carbonate of potash, 0·25 per cent., in water, at 63°	17·2
Carbonate of potash, 10 per cent., in water, at 66°	17·55
Carbonate of soda, 1 per cent., at 61°	17·55
Carbonate of soda, 10 per cent., at 55°	16·85
Sulphate of potash, 1 per cent., at 58°	17·15

	Millimeters.
Sulphate of potash, saturated solution, at 58°	16·3
Sulphate of soda, 1 per cent., at 55°	17·75
Sulphate of soda, 10 per cent., at 58°	16·95
Hydrochloric acid, 1 per cent., at 63°	17·5
Sulphuric acid, 0·1 per cent., at 63°	17·4
Sulphuric acid, 1 per cent., at 63°	16·35
Sulphuric acid, 5 per cent., at 63°	16·65
Sulphuric acid, 10 per cent., at 63°	16·25
Sulphuric acid, undiluted ($HO\,SO_3$), at 63°	8·1
Oxalic acid, 1 per cent., at 66°	17·35
Oxalic acid, 4 per cent., at 62°	17·2
Ammonia, 0·1 per cent., at 66°	16·65
Ammonia, 1 per cent., at 66°	16·15
Ammonia, 12 per cent. (0·943 sp. gr.), at 66°	15·05
Sugar, 10 per cent., at 65°	16·3
Alcohol, 0·8 per cent. (0·9985 sp. gr.), at 60°	15·5
Alcohol, 4·5 per cent. (0·992 sp. gr.), at 63°	13·2
Alcohol, 7·8 per cent. (0·987 sp. gr.), at 60°	11·05
Alcohol, 71 per cent. (0·869 sp. gr.), at 63°	6·

Alcohol falls in the greatest degree below water in capillarity, yet the former substance is one of the least remarkable for the power to occasion osmose.

The newer facts to be related also increase the difficulties of the capillary theory of osmose.

Fig. 1.



My own experiments on osmose were made with both mineral and organic septa.

I. A convenient earthenware or baked clay osmometer is easily formed by fitting a glass tube and cover to the mouth of the porous cylinder, often used as a cell in Grove's battery, as in fig. 1; the cylinder was generally 5 inches in depth by 1·7 inch in width, inside measure, and was capable of holding about six ounces of water. Gutta percha is much preferable to brass as the material for the cap or cover. The glass tube above was also comparatively wide, being 0·6 inch or 15 millimeters in diameter, and was divided into millimeters. It was not more than 6 inches in length. Each of the divisions or degrees amounted approximatively to $\frac{1}{750}$th part of the capacity of the clay cylinder.

In conducting an experiment, the cylinder,[1] always previously moistened with pure water, was filled with any saline solution to the base of the glass tube, and immediately placed in a jar of distilled water, of which the level was kept adjusted to the height of the liquid in the tube of

the osmometer throughout the whole experiment, so as to prevent inequality of hydrostatic pressure. The volume of water in the jar was comparatively large, fifty to eighty ounces. The rise or fall of the liquid in the tube was noted hourly for five hours. This rise commenced immediately, and was pretty uniform in amount for each hour during the short period of the experiment. The object aimed at was to observe the osmose of the solution before its composition was materially altered by dilution and the escape of salt by diffusion. The quantity of salt diffused from the osmometer into the water-jar during the experiment was also observed. After every experiment the osmometer was washed out by distilled water, which was allowed to permeate the porous walls of the cylinder, under the pressure of a column of water of about 30 inches in height, for eighteen hours. All the experiments were made at a temperature between 56° and 64°. The clay osmometer attained a considerable degree of uniformity in its action, when the same saline solution was diffused from it once in each of two or three successive days, with a washing between each experiment. A single observation is not much to be relied upon, as the first experiment often differs considerably from the others. One per cent. solutions were always used when the proportion of salt is not specified. Much larger proportions of salt have hitherto been generally employed, but it was early observed that the osmose absolutely greatest is obtained with small proportions of salts in solution. One part of salt to 400 water gives a higher osmose in earthenware than any other proportion for the great majority of substances. Osmose appeared, indeed, to be peculiarly the phenomenon of dilute solutions.

With the same proportion (1 per cent.) of different substances, the osmose varied from 0 to 80 degrees. Occasionally, instead of a rise of liquid in the tube, a fall was observed; the fall may be spoken of as negative osmose, to distinguish it from the rise or positive osmose.

Soluble substances of every description were tried, and find a place in the following classes:—

1. Substances of small osmotic power in porous earthenware; osmose under 20 of the millimeter degrees (ms.).

This class appears to include nearly all neutral organic substances, such as alcohol, pyroxylic spirit, sugar, glucose, mannite, salicin, amygdalin, salts of quinine and morphine, tannin, urea; also certain active chemical substances, which are not salts nor acids; chlorine water, bromine water.

The great proportion of neutral salts of the earths and metals proper also, belong to the same class, such as chloride of sodium, of which the positive osmose was greatest in a solution containing no more than 0·125 per cent., being 19 ms. with that proportion of salt, but falling off and often becoming slightly negative with 1 per cent. and higher proportions of salt in solution. Chloride of potassium is similar.

Nitrate of soda gave an osmose of 8, nitrate of silver of 18 ms.

The salts of the magnesian oxides are all low and sometimes slightly negative.

Chlorides of barium and strontium both gave 18 ms.; nitrate of strontia, 5 ms.; sulphate of magnesia, 0·5 per cent., 2 ms.; 1 per cent., 2 ms.; 2 per cent., 3 ms.; sulphate of zinc was very similar, +2 to −2 ms., from 0·5 to 2 per cent.; chloride of mercury, 1 per cent., gave 6 and 8 ms. in two experiments.

2. Substances of an intermediate degree of osmotic force; osmose from 20 to 35 degrees. Sulphurous acid gave 20 ms. Certain vegetable acids have a similar osmose. Tartaric acid, in solutions of 0·25, 1 and 4 per cent., gave 24, 26 and 28 ms.; citric acid, 1 per cent., 30 ms. Also monobasic acids, such as hydrochloric acid, nitric acid, acetic acid, have the same moderate osmotic action in porous earthenware.

3. Substances of considerable osmotic power in porous earthenware; osmose from 35 to 55 ms.

In this class are found the polybasic mineral acids: sulphuric acid, 0·5 per cent., gave even 63 ms.; 2 per cent., 54 ms., or nearly the same osmose as the smaller proportion of acid.

In another earthenware cylinder, the following observations on the osmose of sulphuric acid were successively made:—

0·1	per cent.	43 and 43 ms.
1	per cent.	40 and 40 ms.
4	per cent.	41 and 39 ms.
10	per cent.	38 and 39 ms.

The results exhibit much similarity of osmose through a great range (1 to 100) in the proportion of acid. So small a quantity of this acid as 1 part in 1000 water, appears to give as great an osmose as any larger proportion of acid.

Certain neutral salts, sulphate of potash, sulphate of soda, sulphate of ammonia, belong to the same class.

With sulphate of soda the osmose for the different proportions 0·125, 0·25, 1 and 4 per cent. of salt, was 46, 47, 36 and 24 ms. respectively; the osmose diminishing with the increased proportion of salt.

Of sulphate of potash, 0·25 per cent. gave 51 ms.; 1 per cent. 46 ms., and 4 per cent. 38 ms., showing no great change from one quarter to 4 per cent.; chromate of potash, 1 per cent., gave an osmose of 54 ms.

4. Substances exhibiting the highest degree of osmotic power in porous earthenware.

Salts of the alkalies, possessing either a decided acid or alkaline reaction, and certain neutral salts of potash.

Binarseniate of potash gave 66 ms.; Rochelle salt 82 ms.

With binoxalate of potash the osmose observed in an earthenware osmometer was—

For 0·02	per cent.	32 ms.
0·05	per cent.	55 ms.
0·1	per cent.	63 ms.

For 0·25 per cent. . . . . 70 ms. (highest)
1 per cent. . . . . 63 ms.
2 per cent. . . . . 56 ms.

Of salts having alkaline properties, phosphate of soda gave 70·5; borax, carbonate of soda and bicarbonate of soda all gave numbers which ranged above 60 ms. in various osmometers.

To the same class also belong certain strong acids, phosphoric acid giving an osmose of 62 ms., glacial phosphoric acid of 73 ms.

The caustic alkalies have probably too strong a disorganizing action upon the septum to allow osmose to proceed undisturbed. They give a positive osmose when present in a minute proportion, but very soon attain their *terme moyen*, and then become slightly negative.

Caustic soda, 0·01 per cent., gave 24 ms.; 0·02 per cent., 29 ms.; 0·05 per cent., 31 ms., which was the highest osmose observed; 0·1 per cent., 22 ms.; 0·25 per cent., 3 ms.; 1 per cent. and 2 per cent. of caustic soda gave both −10 ms.

It appears most clearly that highly osmotic substances are also chemically active substances. Both acids and alkaline substances possess the affinities which would enable them to act upon the silicates of lime and alumina, which form the basis of the earthenware septum. Lime and alumina were accordingly found in solution after osmose, and the corrosion of the septum appeared to be a necessary condition of the flow.

It was found impossible to exhaust the whole soluble matter of the walls of the earthenware osmometer, by washing, either with water, or with a dilute acid, for the process of decomposition appeared to be interminable. After such washings the action of an osmometer was often greatly modified upon salts of moderate osmose, such as chloride of sodium; and similar changes gradually took place in the osmometers when used in ordinary experiments with saline solutions.

It is on this account that I avoid the lengthened detail of numerous experiments which were made with the earthenware osmometer, and confine myself to general statements.

Further, the potash salts were also largely kept back or absorbed by the earthenware, a phenomenon of the same class as the retention of alkalies by aluminous soils, which has been studied by Messrs. Thomson and Way.

Other septa, which were not acted upon by the salts, were found deficient in osmotic activity, although possessed of the requisite degree of porosity. Gypsum, compressed charcoal, and tanned sole-leather, gave rise to no osmose when permeated by saline solutions. White plastic clay had an osmotic power which was quite insignificant when compared with that of baked clay: now the former may be considered as an aluminous compound, upon which the decomposing action of water has been already exhausted, while the latter is in a form more liable to decomposition, in consequence of an effect of heat upon the constitution of the aluminous silicates of the

clay. A plate of Caen stone, which is an impure limestone, was greatly more active with a solution of carbonate of potash than a plate of pure white marble was. The effect of impurities in making limestone suitable for osmose did not escape the observation of DUTROCHET; it was referred by him to the attraction of alumina for water. Mere capillarity, therefore, is insufficient to produce the liquid movement, while the *vis motrix* appears to be some form of chemical action.

For the proper appreciation of a chemical theory of the osmotic force, I would now invite attention to a purely speculative subject, namely, the molecular constitution of water and saline solutions. Allowing that water, in the state of vapour, is correctly represented as a compound of one equivalent of oxygen and one of hydrogen, it may still be true that the molecule of *liquid water* is a varying aggregate of many such molecules, or is n times HO. But if so much is conceded, a new and peculiar grouping of the atoms of oxygen and hydrogen becomes not only possible but probable. Instead of arranging them in a series of pairs of H+O, H+O in our compound molecule, we may give a binary form to that molecule in which a single atom of oxygen is the negative or chlorous member, and the whole other atoms united together form a positive or basylous radical. In this radical we have a certain multiple of HO with one H in excess, the last condition being most usual in compound radicals, such as methyl, ethyl, benzoyl, &c., which have all a single unbalanced equivalent of hydrogen; $H_n O_n = (H_{m+1} O_m) + O$.

Further, this new oxide should be more easily decomposed than oxide of hydrogen, HO. The basicity of the radical $(H_{m+1} O_m)$ depends upon the disproportion of the equivalents of oxygen and hydrogen in its constitution, there being one of hydrogen in excess. Now that disproportion becomes less as we ascend, as in 3H+2O, 11H+10O, 101H+100O; and the more feeble the basyl-atom, it may be supposed to retain less forcibly its fellow oxygen-atom or other negative element with which it is combined. When water, therefore, has to undergo decomposition in a voltaic circle, it will naturally assume the molecular arrangement supposed, as being the binary form which is most easily divisible into a positive and negative element, or that in which water is most easily decomposed.

This molecular view has been brought forward at present principally for the aid which it gives in conceiving what is known as electrical endosmose.

This interesting phenomenon, first well developed by our colleague Mr. PORRETT, has very lately been defined with great clearness by M. WIEDEMANN*. The water which accumulates at the negative pole (or follows the hydrogen), in the electrolysis of the pure liquid, is found to be exactly proportional to the amount of circulating affinity; that is, with every equivalent of hydrogen that is discharged at the negative pole the same quantity of water arrives there, and will force its way through a porous diaphragm to reach that destination. The reason now suggested is, that the travelling basylous atom in the voltaic decomposition is not hydrogen simply, but

* WIEDEMANN, POGGENDORFF's Annalen, vol. lxxxvii. p. 321.

the voluminous basylous molecule ($H_{m+1}O_m$) above described; which again breaks up at the negative pole into hydrogen and water, $(H_{m+1}O_m)=mHO$ and H.

But even although such a representation of the circumstances of electrical endosmose may not be fully admitted, the phenomenon itself is of great service to us, as showing that in the occurrence of chemical decompositions affecting ultimate particles, sensible volumes of water may be involved and set in motion.

Further, in considering the action of chemical affinity between bodies in solution, between an acid and alkali for instance, we are apt to confine our attention to the principal actors in the combination, and to neglect entirely their associated water of hydration. Yet both the acid and base may have large trains of water attached to them by the tie of chemical union. Sulphuric acid certainly evolves heat with the fiftieth equivalent of water that is added to it, and probably in dilute solution that acid is capable of having a still greater number, indeed an indefinitely large number of equivalents of water combined with it. In fine there is reason to believe that chemical affinity passes, in its lowest degrees, into the attraction of aggregation.

The occurrence of chemical decomposition within the substance of a porous resisting septum may be calculated to bring into view the movement and disposal of the water chemically associated in large quantities with the combining substances; as the interposition of a porous diaphragm in electrical endosmose makes sensible a translation of water in voltaic decompositions which is not otherwise observable.

II. The osmose of liquids has hitherto been principally studied in septa of *animal membrane*, which from their thinness, their ready permeability combined with a sufficient power of resistance to the passage of liquids under pressure, have great advantages over mineral substances.

The great proportion of the experiments of the present inquiry were also made with animal membrane.

The membrane osmometer employed, which is only a modification of the classical instrument of Dutrochet, was prepared as follows:—

Fig. 2.

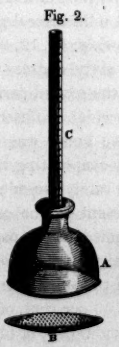
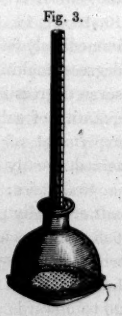


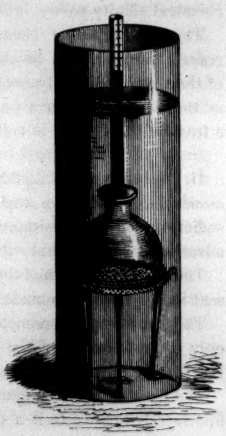
Fig. 3.



The mouth of a little glass bell-jar A (fig. 2) had first loosely applied to it a plate of perforated zinc B slightly convex, and then the membrane was tied tightly over the latter for the sake of support (fig. 3). The quantity of metal removed in the perforations of the zinc plate amounted to 49 per cent. of the weight of the zinc. This plate was always varnished or painted to impede, if not entirely prevent, the solution of the metal by acid fluids. The usual diameter of the bulb was about 3 inches or 75 millimeters, and its capacity equal to 5 or 6 oz. of water. The tube C was usually not more than 6 inches in length, but comparatively wide, its diameter being about 7·5 millimeters, that is one-tenth

of the diameter of the mouth of the bulb, and it was divided into millimeters. The action of an osmometer depends chiefly upon the extent of membrane-surface exposed, and very little upon the capacity of the instrument. Hence the relation of diameters (or areas) between the bulb and tube was adopted in preference to the relation in capacity, the area of a section of the tube being one-hundredth of the area of the disc of membrane, or rather it was reduced by calculation to this relation by means of a coefficient for each instrument. Hence a rise of liquid in the tube amounting to 100 millimeters, indicates the admission into the bulb of a sheet of water of 1 millimeter (one twenty-fifth part of an inch) in depth, over the whole surface of the membrane, and so in proportion for any other rise in the tube. These millimeter divisions (ms.) of the tube mark therefore degrees of osmose which have an absolute and equal value in all instruments. The bulb of the instrument filled with the solution to be operated upon was placed within a cylindrical glass jar of distilled water, containing at least sixty ounces (fig. 4), and during the experiment inequality of hydrostatic pressure was carefully avoided by maintaining the surface of the water in the jar at the level of the liquid in the tube. The osmometer was supported upon a tripod of perforated and painted zinc, at a height of about 4 inches from the bottom of the glass cylinder. The osmose was observed hourly for five hours, during which time it advanced in general with considerable uniformity. In an experiment with fresh ox-bladder as the septum and a solution of 1 per cent. of carbonate of potash in the osmometer, the rise, in five consecutive hours, was 10, 12, 11, 14, 13 millimeter degrees, and in five hours immediately following, 13, 12, 9, 11 and 12 millimeter degrees, making sixty degrees in the first, and fifty-seven degrees in the second period of five hours. The quantity of salt which diffused outwards during the experiment of five hours was also frequently determined, usually by evaporating the liquid of the water-jar to dryness; it rarely exceeded one-tenth part of the salt originally present in the osmometer. The membrane itself was also weighed before it was applied to the osmometer, and again when its use was discontinued, which was generally after six or eight experiments had been made with the membrane. A loss of the substance of the membrane was always observed, varying from 20 to upwards of 40 per cent. of its original weight.

Fig. 4.



The outer muscular coat of bladder soon becomes putrescent, and from changes in its consistence, and the large quantity of salts and other soluble substances which it yields by decomposition, gives occasion to much irregularity in the experiments. The great change in the amount of osmose often produced by merely turning the mem-

brane, observed by M. Matteucci and others, depends often, I believe, upon the soluble matter of the muscular coat being thrown outwards or inwards, according as the membrane is applied. The muscular coat was on this account removed from the ox-bladder employed, and the serous membrane remaining found to acquire greatly increased activity, and also to act with much greater regularity in successive experiments. The membrane so prepared could be used for weeks together without the slightest putrescence of any part of it. Two of these thin membranes, or a double membrane, was often applied. The weight of a disc of single membrane, $4\frac{1}{2}$ inches in diameter in a dry state, varied from about 0·5 to 1·2 gramme. The soundness of the membrane of an osmometer and its degree of permeability were always roughly tested before an experiment, by filling the bulb, without its tube, completely with water, hanging it up in air, and observing how frequently a drop fell from the instrument. The time between each drop varied, with suitable membranes, from one to twenty minutes. The times in which water permeated the same membranes by osmose varied between much narrower limits, perhaps from one to two.

The quantity of salt which traversed different membranes by diffusion, was also found to be in proportion to the osmotic permeability of the membranes, and not to their mechanical porosity.

To wash the membranes, they were macerated in distilled water after every experiment for not less than eighteen hours, without being ever removed from the glass bulb. A membrane also was never allowed to dry, but was kept humid as long as it was in use for experiments.

Osmose in membrane presented many points of similarity to osmose in earthenware. The membrane was constantly undergoing decomposition, soluble organic matter being found both in the fluid of the osmometer and in the water of the outer jar after every experiment; and the action of the membrane appeared to be exhaustible, although in a very slow and gradual manner. Those salts and other substances, of which a small proportion is sufficient to determine a large osmose, are, further, all of the class of chemically active substances, while the great mass of neutral organic substances and perfectly neutral monobasic salts of the metals, such as the alkaline chlorides, possess only a low degree of action.

When a solution of the proper kind is used in the osmometer, the passage of fluid proceeds with a velocity wholly unprecedented in such experiments. Take, for instance, the rise in five hours exhibited in a series of experiments upon solutions of several different proportions of carbonate of potash, made in succession with the same membrane in the order in which they are related.

With 0·1 per cent. carbonate of potash, a rise of 182 ms.
With 0·1 per cent. carbonate of potash, a rise of 120 ms.
With 0·1 per cent. carbonate of potash, a rise of 199 ms.
With 0·5 per cent. carbonate of potash, a rise of 246 ms.
With 0·5 per cent. carbonate of potash, a rise of 194 ms.
With 1 per cent. carbonate of potash, a rise of 205 ms.
With 1 per cent. carbonate of potash, a rise of 207 ms.

Or the rise in the same time with another membrane which had been previously exposed to a steam heat of 212° for ten minutes without impairing its activity.

With 1 per cent. carbonate of potash at 60° Fahr., a rise of 402 ms.
With 0·1 per cent. carbonate of potash at 60° Fahr., a rise of 196 ms.
With 0·1 per cent. carbonate of potash at 60° Fahr., a rise of 153 ms.
With 2 per cent. carbonate of potash at 60° Fahr., a rise of 511 ms.
With 4 per cent. carbonate of potash at 60° Fahr., a rise of 781 ms.
With 10 per cent. carbonate of potash at 60° Fahr., a rise of 863 ms.

In the last experiment a rise of fluid in the tube of upwards of 30 inches occurs in five hours, and so much water is impelled through the membrane as would cover its whole surface to a depth of 8·6 millimeters, or one-third of an inch. Both membranes, but particularly the first, show the comparatively great activity of small proportions of salt, the average osmose of 0·1 per cent. of carbonate of potash in the first osmometer being 167 millimeter degrees, and of 1 per cent. 206 millimeter degrees.

Now the quantity of carbonate of potash which diffuses out of the osmometer into the water-jar, was determined by the alkalimetrical method in the second and third of the 0·1 per cent. observations first related, and found to be in both cases 0·018 gramme (0·28 grain); the quantity of water also which entered in return can be calculated from the known capacity of the tube of the osmometer, of which each millimeter division represented 0·060 gramme of water; and consequently 167 divisions represent 10·020 grammes (155 grains) of water. We have, in 0·1 per cent. solution,

Mean diffusate of carbonate of potash . . .	0·018 gramme	= 1
Mean osmose (of water)	10·020 grammes	= 556

The conclusion is, that while the membrane was traversed during the five hours of an experiment by 1 part of carbonate of potash passing outwards, it was traversed by 556 parts of water passing inwards.

In the two experiments with 1 per cent. solution of carbonate of potash in the same osmometer, the diffusates were 0·192 and 0·198 gramme of carbonate of potash, which are sensibly ten times greater than the diffusates of the 0·1 per cent. solution. But the mean osmose of the 1 per cent. solutions is greater than that of the 0·1 per cent. solutions only in the proportion of 206 to 167, or as 1 to 0·81. The ratio in question however varies greatly in different membranes. We have, consequently, in 1 per cent. solution,—

Mean diffusate of carbonate of potash . . .	0·195 gramme	= 1
Mean osmose (of water)	12·360 grammes	= 63·4

Whatever, therefore, be the nature of the chemical action occurring in the membrane which influences osmose, a minute amount of that action appears to be capable of producing a great mechanical effect.

All idea of contractility or organic structure being the foundation of the osmotic

action of membrane, was excluded by the observation that similar large effects could be obtained from a septum of pure coagulated albumen.

A convenient albumen osmometer is constructed by covering the opening of the bulb of the former instrument by ordinary thin cotton calico, which is best applied wet, and painting over the outer surface of the calico two or three times with undiluted egg albumen, an hour being allowed to elapse between each application of the albumen. The instrument is then suspended in the steam rising from boiling water for a few minutes, so as to completely coagulate the albumen. The albuminated calico may then be macerated for twenty-four hours before use, by placing the osmometer in cold water, to dissolve out the soluble salts of the albumen. It should be preserved always in a humid state. Before application to the calico, the albumen in many cases was neutralized with acetic acid and filtered, the more completely to obliterate every trace of organic structure.

The osmose in a particular instrument of this kind was, at 50°, for

1	per cent. carbonate of potash . . .	211 ms.
1	per cent. carbonate of potash . . .	367 ms.
1	per cent. carbonate of potash . . .	387 ms.
0·1	per cent. carbonate of potash . . .	127 ms.
0·1	per cent. carbonate of potash . . .	124 ms.

The correct rate is rarely obtained in the first observation, as seen above, in osmometers of albumen as well as of other materials.

The albumen plate has generally a greater thickness than prepared membrane, which appears to diminish proportionally the quantity of salt which escapes by diffusion.

The diffusate in the three experiments above of 1 per cent. carbonate of potash was 0·024, 0·038 and 0·042 gramme of the salt. The largest proportion of carbonate of potash (0·042 gramme) which was obtained in the last of the three experiments was replaced by 23·220 grammes of water, or 552 times the weight of the salt.

An obvious and essential condition of osmose is difference of composition in the two fluids in contact with the opposite sides of the porous septum. With the same solution, or with pure water, in contact with both surfaces of a membrane there may be chemical action, but it will be equal on both sides, and although probably attended with movements of the fluids, yet nothing will be indicated, as the movements, being equal and in opposite directions, must neutralize each other. Difference of composition in the two fluids is necessary in order that there may be inequality of action upon the two sides of the membrane. It is difficult however, with respect to the chemical action, to ascertain either its true sphere or its exact nature. No substance appears to be permanently deposited in the membrane during osmose, even by easily decomposed metallic salts, such as salts of lead and mercury. The action upon the membrane is probably of a solvent nature, and its seat may possibly be ascertainable

when two membranes are used together. Some observations made on the comparative loss of weight of the outer and inner membrane have not, however, shown any remarkable difference. But this again may arise from the great proportion of the loss in both membranes being due to the ordinary solvent action of water alone, and the operative solvent action of the osmotic salt being comparatively minute in amount; or it may depend, and I am most inclined at present to take this view, upon the chemical actions being of a different kind on the two sides of the membrane, and not upon the inequality simply of one kind of action. Such a supposition was suggested by the fact, which will immediately appear, that osmotic activity and easy decomposition are properties often found together in binary compounds. The basic and acid agents then developed are both capable of acting upon albuminous septa. We may imagine, for instance, in the osmotic action of a neutral salt, the formation within the thickness of the septum of a polar circle, one segment of which (composed of the binary molecules of the salt) presents a basic molecule to the albumen at the inner surface of the septum, and an acid molecule to the albumen at the outer surface, the circle being completed through the substance of the septum which forms the second segment. Both surfaces of the septum would be acted upon, but at one side we should have combination of the albumen with an alkali, on the other side with an acid. This however must be taken as a purely ideal representation of the condition of the septum in osmose. I have not discovered such a polar condition of the septum, and I doubt whether the galvanometer could be properly applied to exhibit it, as the placing of the poles of that instrument in the dissimilar fluids existing on opposite sides of the septum would alone be sufficient to give rise to voltaic polarization. At present I must confine myself to the enunciation of certain general empirical conclusions respecting the operation of chemical affinity in osmotic experiments.

With animal septa, frequent examples of the outward flow of liquid from the osmometer present themselves, causing the liquid column to fall instead of rise in the tube. This phenomenon (exosmose) I have spoken of as negative osmose. The observation of Dutrochet, that oxalic acid in the osmometer, and also tartaric acid at a certain point of concentration, give rise to negative osmose, I have been able to generalise in so far as acids have universally either a negative osmose, or lie at the very bottom of the positive class.

Oxalic acid gave in membrane, for 1 per cent. acid, −148 ms. and −141 ms.; and for 0·1 per cent., −10 and −27 ms. In another membrane, 1 per cent. of the same acid alone gave −136 ms.; with the addition of 0·1 per cent. hydrochloric acid, −181 and −168 ms. By the addition of 0·1 per cent. of chloride of sodium, a salt which in small proportions is nearly neutral to osmose, the negative osmose of 1 per cent. oxalic acid fell in the same membrane to −45 ms., and with the addition of 0·25 per cent. of chloride of sodium the osmose was +6 ms., or became slightly positive. The negative osmose of 1 per cent. of oxalic acid, in a membrane where it amounted to −56 and −57 ms. in two experiments, became, with the addition of 0·1 per cent.

of albumen −46 ms.; of 0·25 per cent. of albumen −20 ms.; of 0·25 per cent. of gelatin −59 ms., and of 0·25 per cent. of sugar −53 ms.

In albuminated calico, the osmose of 1 per cent. of oxalic acid was also negative, namely −13, −16 and −20 ms. in three successive observations. With the addition to the oxalic acid of 0·1 per cent. hydrochloric acid, the osmose became −46 and −58 ms.; and with the addition of 0·1 per cent. of sulphurous acid, the osmose became −62 and −58 ms.

Of *hydrochloric acid* introduced into the membrane-osmometer in the small proportion of 0·1 per cent., the negative osmose was −92, −37 and −27 ms. in three successive experiments. The negative osmose of hydrochloric acid was still more powerfully counteracted than that of oxalic acid, by the association of a minute proportion of chloride of sodium with the acid. The negative osmose of this acid appears to be extremely precarious. It is reversed by a great variety of neutral soluble substances, and on that account can rarely be observed at all with bladder undivested of its muscular coat.

In a certain prepared membrane, *sulphuric acid*, 0·1 per cent., gave an osmose of −4, +8 and +7 ms.

Nitric acid, 0·1 per cent., gave an osmose, at 58°, of +8 and +23 ms.

Tribasic phosphoric acid, 1 per cent., gave −6 and −7 ms., at 61° and 63°. The diffusates of phosphoric acid, in the same experiments, amounted to 0·143 and 0·130 gramme.

The *glacial or monobasic phosphoric acid*, 1 per cent., gave +137 and +131 ms., at 55°, which is a considerable positive osmose, an interesting circumstance when taken in connexion with the deficient acid character of that modification of phosphoric acid. The same acid, 0·1 per cent., gave a positive osmose in the last membrane of 28 and 23 ms.

Citric acid, 1 per cent., gave 39 and 36 ms.; 31 and 31 ms., at 62°; the first in membrane and the second in albumen.

The same acid, 1 per cent., after being fused by heat, gave, at 63°, −38 and −35 ms. in membrane; 0 m. and −2 ms. in albumen.

A small proportion of fused citric acid, 0·1 per cent., gave on the other hand a slight positive osmose, namely 15 ms. and 2 ms. in the previous membrane and albumen osmometers respectively.

Tartaric acid, 1 per cent., gave 18 and 19 ms. in membrane, at 68°; with 20 ms. in albumen, at 62°.

The same acid, after being fused by heat, gave −68 and −61 ms. in membrane, at 57°, showing a molecular change from fusion, as in citric acid.

The diffusate in the last two experiments was 0·123 grm. and 0·132 grm. of acid.

In albumen the osmose of fused tartaric acid remained slightly positive, being 5 and 2 ms. for 1 per cent., at 60°, and 5 and 3 ms. for 0·1 per cent., at the same temperature.

Racemic acid, 1 per cent., gave 4, 11 and 7 ms. in three experiments, at 55°, in the last used membrane; with 15 and 22 ms. at the same temperature in albumen; or was always slightly positive like tartaric acid.

Acetic acid, in the proportions of 0·1, 0·5 and 1 per cent., gave sensibly the same small positive osmose, 25 to 28 ms., at 57° to 62°, in membrane.

A saturated solution of *carbonic acid* in water gave 25 and 26 ms. in membrane, with 20 and 22 ms. in albumen, both at 65°.

The last solution, diluted with an equal bulk of water, gave an osmose of 15 and 18 ms. in membrane, and 16 ms. twice in albumen, both at 63°.

Terchloride of gold is negative in its osmose like the stronger acids, giving −49 and −54 ms. in membrane, at 64°, with much reduction of metallic gold in the substance of the membrane.

Bichloride of platinum, made as neutral as possible by evaporation, gave for the 1 per cent. solution −32 and −30 ms. in membrane, at 61°. For the 0·1 per cent. solution, a positive osmose of 27, 14 and 5 ms. in three successive experiments made with the last membrane, at 64°, 65° and 62°. The same 1 per cent. solution gave in albumen, at 61°, a positive osmose of 54 and 50 ms.; the 0·1 per cent. solution also, at 64°, gave 43 ms. Albumen appears thus to be less adapted for bringing out the negative osmose of various substances than membrane is.

In membrane, *bichloride of tin*, 0·1 per cent., gave −24 ms., at 61°; 1 per cent. −46 and −71 ms., at 59°. The addition to the last of 0·5 per cent. of sulphuric acid gave −63 ms., or did not alter the character of the osmose. But partial neutralization of the 1 per cent. tin solution, by ammonia, on the other hand, gave 0 m., or destroyed all osmose. One per cent. of bichloride of tin gave only a small negative osmose in albumen, namely 5 ms. twice, at 59°.

Oxalic acid carries the highly negative character of its osmose into the *binoxalate of potash*, of which 1 per cent. of anhydrous salt gave in membrane −112 and −99 ms., at 62°; 0·1 per cent., −30 ms., at 60°. One per cent. of the same salt in albuminated calico gave −20 ms., at 60°. A saturated solution of binoxalate of potash, containing 2·5 per cent. of salt, gave −15 ms. in the last osmometer.

Bisulphate of potash, 1 per cent., gave 4 and 7 ms. in membrane, at 56°; in albumen, 7, 3 and 6 ms., at 56°.

A solution of *bitartrate of potash*, saturated in the cold, also gave a small positive osmose, namely 4 and 2 ms. in membrane, and 20 and 17 ms. in albumen, both at 56°. Other supersalts tried gave also a small positive osmose, such as binarseniate of potash and bichromate of potash. It becomes doubtful therefore whether any of the supersalts of potash are negative, except the acid oxalates of that base.

Neutral organic substances dissolved in water appear to be generally deficient in the power to give rise in membrane to that osmose which depends upon a small quantity of the soluble substance, such as 1 per cent., or a still less proportion. The osmose obtained in ox-bladder employed without removing the muscular coat, was,

in 1 per cent. solutions of the substances, salicin 5 ms., tannin 3 ms., urea 4 ms., gelatin 9 ms., amygdalin 6 ms., lactine 7 ms., glucose 7 ms., gum-arabic 18 ms., and hydrochlorate of morphine 4 ms.

The relations to osmose of alcohol and sugar were more fully examined. With these and other chemically inactive substances, the osmose, although small for 1 per cent., increases progressively with larger proportions of the substance, and also bears a close relation to the proportion of substance diffused outwards, circumstances which give a mechanical character to the osmose. It is with such substances that the influence of diffusibility upon osmose is most likely to betray itself. They have a peculiar interest in the study of the phenomenon, as they present a certain small but remarkably uniform amount of osmose without the known intervention of any strong chemical affinities.

Alcohol.—In describing an experiment I shall endeavour to put forward all the circumstances which can be supposed to influence in any way the result.

In the table which follows, Column I. contains the proportion of absolute alcohol, by weight, which is dissolved in the water of the osmometer.

A 10 per cent. solution is prepared by weighing 10 grammes of the substance, and then adding water to it so as to make up the liquid to the volume of 100 grammes of water. It is necessary to make up in this way solutions used in experiments of diffusion and osmose, in order to preserve a true relation in solutions containing the different proportions of substance, for it is a fixed volume (not weight) of these solutions which must be used in the osmometer. We come thus to have with a 20 per cent. solution of alcohol exactly twice as much alcohol in the osmometer as with a 10 per cent. solution of alcohol, and so of other proportions.

The membrane of the osmometer is always to be considered as fresh, or as used for the first time in the first experiment narrated, and the observations to be made successively as they stand in the table. The length of maceration in cold water to which the membrane has been exposed previous to the osmotic experiment, as before described, is given in Column V. By the most frequent time of one day is to be understood the space of eighteen hours, which intervened between experiments on successive days.

The hydrostatic resistance of the membrane given in Column VI. is the length of time, in minutes, observed to elapse between the fall of two drops from the bulb of the osmometer filled with distilled water, and hung up in air as already described. The temperature of the water in the glass cylinder during the experiment is noted in Column VII.; the rise of fluid in the tube of the osmometer or osmose, in millimeter divisions of the tube, appears in Column II., and the absolute amount of the same osmose is expressed in Column III. in grammes, or more strictly in gramme measures of water. Lastly, the weight of diffusate found in the water of the glass cylinder appears in Column IV. These last two data, the osmose and diffusate, both in grammes, afford the means of comparing the weight of substance which has

escaped from the osmometer with the weight of water which has entered the osmometer in the same time. It is necessary however to recollect, that the apparent osmose or rise observed, is only the excess in volume of the liquid which has entered over the volume of the liquid which has left the osmometer. To obtain the full volume of water which has entered (the true osmose), it is therefore necessary to add the bulk of the substance diffused to the osmose observed.

Table I.—Alcohol in Osmometer A of double membrane during five hours.

I. Alcohol in solution.	II. Rise or osmose in millimeter degrees.	III. Rise or osmose in grammes of water.	IV. Diffusate of alcohol in grammes.	V. Previous maceration of membrane.	VI. Hydrostatic resistance of membrane.	VII. Temperature, Fahr.
per cent.				days.	min.	°
0·25	12	.....	.....	1½	8	63
0·25	7	.....	.....	1	8	63
1	10	.....	.....	1	6	66
1	15	.....	.....	1	6	66
2	20	.....	.....	1	6	67
2	22	.....	.....	1	6	69
5	45	1·984	0·521	2	6	72
5	45	1·984	0·452	1	8	70
10	70	3·072	.....	1	8	67
10	76	3·328	.....	1	8	67
20	107	4·672	.....	1	8	67
20	109	4·800	.....	1	8	67

A second series of observations was made simultaneously, in another membrane osmometer, in order to ascertain the degree of concordance to be expected in such experiments.

Table II.—Alcohol in Osmometer B of double membrane for five hours.

I. Alcohol in solution.	II. Rise or osmose in millimeter degrees.	III. Rise or osmose in grammes of water.	IV. Diffusate of alcohol in grammes.	V. Previous maceration of membrane.	VI. Hydrostatic resistance of membrane.	VII. Temperature, Fahr.
per cent.				days.	min.	°
1	14	.....	.....	2½	12	63
1	14	.....	.....	1	12	63
2	19	.....	.....	1	8	66
2	19	.....	.....	1	8	66
5	46	.....	.....	1	8	67
5	54	2·432	0·579	1	8	69
10	90	4·028	1·505	2	6	72
10	96	4·332	.....	1	8	70
20	120	5·396	.....	1	8	67
20	123	5·472	.....	1	4	67
20	137	6·156	.....	1	4	67
20	142	6·384	.....	1	4	67

It will be observed that the osmose increases with the proportion of alcohol, but not in so rapid a ratio; the osmose of the 20 per cent. solution being about only ten

times greater than that of the 1 per cent. solution in both series. The hydrostatic resistance of the membrane B falls off in a remarkable manner in the later experiments, indicating an increased facility of permeation, which may influence the increased osmose in the last two observations of this series. The results otherwise of the two series exhibit a fair amount of correspondence, both in the degree of osmose and the amount of diffusate for the same proportions of alcohol in the two osmometers. It should be added, that in several instances the water in the jars was changed after the third hour of the experiment, with the higher proportions of 10 and 20 per cent. The alcohol was determined, after it had been concentrated by two distillations, by means of DRINKWATER's table of densities.

Several experiments were made to determine the proportion of the diffusate of alcohol from 5 and 20 per cent. solutions respectively of that substance, in membrane osmometers. The mean proportion was as 1 to 3·02, which is mentioned here, as I was led at first to a different conclusion by earlier and imperfect experiments.

Sugar.—The osmose of sugar in membrane was examined very fully, in the hope that the simple effect of diffusion would be exhibited without being modified by any chemical action, in a substance so entirely neutral.

Crystallized cane-sugar was made use of.

TABLE III.—Sugar in Osmometer D of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Sugar in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of sugar in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				days.	min.	°
1	21	1·027	.....	1	4	64
1	8	0·395	0·150	9	2½	63
1	19	0·948	0·140	1	3½	63
2	19	0·948	0·178	1	2½	66
2	19	0·948	0·182	1	2½	66
5	39	1·900	0·438	1	2½	67
5	49	2·370	0·480	1	2½	69
10	66	3·239	1·110	2	2½	72
10	79	3·871	0·853	1	2½	70
10	76	3·713	0·840	1	3	67
20	121	5·975	1·376	1	3	67
20	117	5·688	1·485	1	3	67

It was very desirable to find whether the deviations from a regular progression seen in the numbers for the osmose and diffusate in the preceding results are essential, or accidental and peculiar to the present membrane. It was also desirable to find whether a membrane would stand the repetition of such a series of experiments and continue to give similar results. A double series of experiments were accordingly made with new membrane.

TABLE IV.—Sugar in Osmometer E of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Sugar in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of sugar in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				days.	min.	°
0·25	5	0·240	.....	2	10	63
0·25	9	0·420	0·050	1	10	63
1	12	0·531	0·110	1	8	66
1	11	0·472	0·106	1	10	66
2	24	1·060	0·205	1	8	67
2	31	1·357	0·208	1	8	69
5	65	2·891	0·600	2	8	72
5	63	2·773	0·555	1	8	70
10	89	3·953	1·073	1	10	67
10	104	4·602	0·967	1	10	67
10	96	4·248	.....	1	10	67
20	133	5·900	1·457	1	10	67
20	106	4·720	1·643	10	10	64
20	118	5·251	1·656	1	6	64
1	19	0·826	0·105	1	6	68
1	19	0·826	.....	1	6	65
2	24	1·062	0·153	1	6	65
2	25	1·121	0·162	1	6	64
5	37	1·652	0·435	2	8	66
5	33	1·425	0·470	1	8	67
10	69	3·068	0·757	2	8	67
10	76	3·363	.....	1	8	69
20	110	4·807	.....	1	8	70
20	112	4·956	1·540	2	3	70

The diffusates of sugar (Column IV.) were obtained by evaporating the fluid of the water-jar to dryness, at 212°, and therefore contain organic matter dissolved out of the membrane; the weight of each of the diffusates is increased by this addition a few thousandths, but not in such a quantity as to affect the result to an extent that is at all material, except in the first diffusate recorded, that from the 0·25 per cent. solution.

Although the results exhibit several irregularities, yet starting from the 1 per cent. observation, in the first series of Table IV., the amount both of osmose and diffusate appears compatible with an arithmetical progression in the observations from 1 to 10 per cent. Thus the average rise in the 1 per cent. solution is 11·5 millimeter degrees, and in the 10 per cent. solution 96·3 ms.; the average diffusate in the 1 per cent. solution is 0·108 gramme, and in the 10 per cent. solution 1·020 gramme.

But with the 20 per cent. solution both osmose and diffusate fall off greatly, and the osmose more than the diffusate. The osmose of the 20 per cent. solution may be taken as 125 ms.,—the mean of the first and third observations, 133 and 118, the intermediate observation 106 being obviously exceptional, possibly from the unusually long maceration of the membrane immediately preceding that experiment. Hence the osmose only rises from 96·3 ms. to 125 ms., while the proportion of sugar in the osmometer was increased from 10 to 20 per cent.

The mean diffusate of sugar also increases with the same change only from 1·020 gramme to 1·585 gramme.

In the second series of observations with the same membrane, given in the lower part of the same Table, both the osmose and diffusate fall off, to an extent which is perhaps pretty fairly represented by the 10 per cent. solution, which gives a mean osmose of 72·5 ms. against 96·3 ms. in the former series, and a diffusate of 0·757 gramme against 1·020 gramme in the former series. A rough proportionality between the two series of observations is sufficiently indicated.

Two observations are recorded in the last series which must not be allowed to mislead. These are the comparatively high osmose of 19 ms. for the 1 per cent. solution, which is accidental, and arises from the 1 per cent. experiments having been immediately preceded by the high proportion of 20 per cent. The other observation referred to is the high diffusate of the last 20 per cent. solution at the bottom of the table, which has no doubt been occasioned by the sudden diminution in the hydrostatic resistance of the membrane from 8 to 3 in that which is the last experiment of the series. The membrane, indeed, appears to be giving way after its long use, for the osmometer had been exposed to the action of water for thirty-five days without intermission.

The reason why the diffusion and osmose are smaller in the second series of experiments than in the first series (nearly as 3 to 4), is (I believe), that the membrane softens and swells somewhat by the protracted action of water; a change in the structure of the membrane which impedes diffusion by increasing the length of the channels through which the salt has to travel.

It may now be interesting to discover the proportion between the water which enters and the sugar which leaves the osmometer in these experiments. That proportion appears not to vary greatly in the range from the 1 to the 10 per cent. solution. For a mean result, the sum of the eight diffusates between 1 and 10 per cent. inclusive, in the first series of observations of Table IV., may be taken, and the osmose belonging to the same experiments. There is so obtained 3·824 grammes of sugar diffused against an osmose of 17·639 grammes of water. But this, the apparent osmose, has to be increased by the bulk of the sugar diffused, which may be estimated at ten-seventeenths of its weight of water, or 2·25 grammes. Adding the last quantity to 17·639 grammes, we obtain—

Sugar or diffusate	3·824 grm. = 1
Replacing water	19·889 grm. = 5·2

Hence the sugar appears to be replaced in osmose by rather more than five times its weight of water. The less complete experiments with alcohol, previously described, indicate a nearly similar relation to its replacing water.

Calculating, in like manner, the observations made upon each of the five proportions of sugar in Table III., we obtain numbers for the replacing water which oscil-

late about the general result first stated; the mean diffusates of sugar and amounts of replacing water were in the different solutions:—

In 1 per cent. solution, 0·145 grm. sugar to 0·756 grm. water . . 1 to 5·21
In 2 per cent. solution, 0·180 grm. sugar to 1·054 grm. water . . 1 to 5·85
In 5 per cent. solution, 0·459 grm. sugar to 2·405 grm. water . . 1 to 5·22
In 10 per cent. solution, 0·934 grm. sugar to 4·158 grm. water . . 1 to 4·43
In 20 per cent. solution, 1·430 grm. sugar to 6·672 grm. water . . 1 to 4·66

The mean of the various solutions is 1 part of sugar replaced by 5·07 water.

The phenomenon of the osmose of sugar partakes very much of a physical character, and may possibly prove to be nothing more than the exchange of sugar for water by the purely mechanical operation of diffusion.

A third series of observations on sugar were made in an osmometer of albuminated calico. The results, it will be seen, are quite in accordance with those of the membrane osmometers.

TABLE V.—Sugar in Osmometer F of Albuminated Calico for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Sugar in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of sugar in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				day.	min.	°
1	16	0·684	0·124	1	2	59
1	22	0·912	0·156	1	10	60
4	31	1·311	0·476	1	1	61
4	42	1·767	0·505	1	1	63
4	34	1·425	0·542	1	1	63
10	92	3·876	1·283	1	0·50	63
10	106	4·389	1·179	1	0·66	64
10	90	3·762	1·193	1	1	63

This osmometer is remarkable for the variable but generally very small amount of its hydrostatic resistance, a condition of the septum which is apt to increase the diffusate, owing to the expulsion of a portion of the solution by the pressure of the dense solution. The diffusates of sugar (Column IV.) may be considered as nearly proportional to the per-centage of sugar in the osmometer. The osmose of the 4 and 10 per cent. solutions are also nearly proportional, the means being 36 and 96 ms.; but the osmose of the 1 per cent. solution is sensibly in excess. A slight excess in the early experiments with an albumen osmometer is, it may be remarked, not unusual, and appears to be due to the considerable quantity of soluble matter, with an alkaline reaction, which the fresh albumen affords to the water in the osmometer, this soluble matter then acting as an osmotic body.

Sulphate of Magnesia.—This salt was selected to illustrate the osmose of neutral salts. The sulphate of magnesia is neutral to test-paper. It appears, further, to be

incapable of passing into the condition of a stable supersulphate or subsulphate by combining with an excess of either acid or base, and is not decomposed in diffusion. Such properties secure to a salt a remarkable indifference, or absence of chemical activity, and recommend sulphate of magnesia for our present purpose.

In a fresh double membrane, 1 per cent. of sulphate of magnesia (anhydrous) gave the small osmose of 13 and 14 ms., at 63°, in two experiments.

A full series of observations was made by means of the osmometer F, used above with sugar, but with the osmotic septum of course changed.

TABLE VI.—Sulphate of Magnesia in Osmometer F of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Sulphate of magnesia (anhydrous).	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				days.	min.	°
2	30	1·254	.....	2	10	72
2	33	1·368	0·265	1	10	70
5	73	3·078	0·540	1	10	67
5	76	3·192	0·553	1	10	67
10	152	6·384	1·020	1	10	67
10	134	5·529	0·962	1	10	67
20	238	9·918	1·623	10	15	64
20	283	11·836	1·687	1	3·5	64
1	23	0·969	0·119	1	5	68
1	20	0·855	0·120	1	5	65
2	30	1·254	0·227	1	5	65
2	29	1·197	0·233	1	5	64
5	69	2·907	0·490	2	6	66
5	68	2·850	0·485	1	6	67
10	132	5·529	0·959	2	6	67
10	140	5·871	0·845	1	6	69
20	277	11·628	.....	1	6	70
20	291	12·198	2·012	2	6	70

The diffusate increases in a somewhat less ratio than the proportion of salt in the osmometer in both of the two series of observations contained in the preceding Table. But a similar falling off in the amount of diffusate from the higher proportions of salt takes place in the diffusion of the same salt, from open phials, as appeared in former experiments on the diffusion of sulphate of magnesia*.

The different solutions then operated upon, and the ratio between the diffusates they gave, were as follows:—

Solutions of sulphate of magnesia diffused .	2	4	8	16	24 per cent.
Ratio of diffusate of these solutions . . .	2	3·671	6·701	11·785	15·678

* Philosophical Transactions, 1850, p. 822.

The proportions of sulphate used in the present osmotic experiments were different, but ratios may be found for them by interpolation, and are given below. We are thus enabled to make the following comparison of the diffusion from different proportions of sulphate of magnesia: (1) in the absence of membrane; (2) in the first series of osmotic experiments given in the preceding Table; (3) in the second series of observations of the same Table:—

Sulphate of magnesia in solution	2	5	10	20 per cent.
(1) Ratio of diffusates without membrane . .	2	4·43	8·21	13·73
(2) Ratio of diffusates with membrane . . .	2	4·12	7·48	12·5
(3) Ratio of diffusates with membrane . . .	2	4·24	7·82	17·34

If the last number (17·34) given for the 20 per cent. solution of the later osmotic series be excluded, and it is manifestly in considerable excess from some accidental cause, the three sets of ratios must be allowed to exhibit considerable agreement.

The membrane appears to have a slight effect in reducing the diffusates of the higher proportions of salt; and this reduction is greater in the early experiments (2) than in the late experiments (3), made with the same osmometer. The comparative diffusion of different proportions of sulphate of magnesia appears, therefore, not to be much deranged by the intervention of membrane.

The average osmose of sulphate of magnesia likewise exhibits a pretty uniform progression. In the first series of experiments of Table VI., we find for the different proportions of salt in solution an osmose of 31·5, 74·5, 143 and 260·5 ms.; numbers which are in the ratio given below:—

Sulphate of magnesia in solution	2	5	10	20 per cent.
Ratio of osmose (first series of experiments) .	2	4·73	9·08	16·54

In the later experiments of the same Table, the different proportions of salt (omitting the first and last proportions) give an average osmose of 29·5, 68·5 and 136 ms., of which the ratios may be stated as follows:—

Sulphate of magnesia in solution	2	5	10 per cent.
Ratio of osmose (second series of experiments) . .	2	4·64	9·22

The osmose appears here to follow more closely in its value the proportion of salt in solution than the diffusate can be said to do, either in open vessels or through membrane; so far, therefore, the osmose and diffusate do not preserve a constant proportion to each other with this salt.

No correction need be applied to the observed osmose of sulphate of magnesia, as this salt does not sensibly increase the bulk of the water in which it is dissolved. The weight of diffusate in Column IV. may, therefore, be immediately compared with the weights of water in Column III. It then appears that in the first series of the osmotic observations in the Table—

In 2 per cent. solution, 1 sulphate of magnesia is replaced by 5·16 water.
In 5 per cent. solution, 1 sulphate of magnesia is replaced by 5·74 water.
In 10 per cent. solution, 1 sulphate of magnesia is replaced by 6·01 water.
In 20 per cent. solution, 1 sulphate of magnesia is replaced by 6·57 water.

According to the average of the whole proportions, sulphate of magnesia is replaced by 5·87 times its weight of water.

While in the later observations of the same Table—

In 2 per cent. solution, 1 sulphate of magnesia is replaced by 5·33 water.
In 5 per cent. solution, 1 sulphate of magnesia is replaced by 5·9 water.
In 10 per cent. solution, 1 sulphate of magnesia is replaced by 6·32 water.

According to the average of the whole proportions of salt in these later observations, sulphate of magnesia is replaced by 5·85 times its weight of water.

The want of uniformity exhibited above in the relation between the quantities of water and salt goes some way to prove that the osmose of sulphate of magnesia in membrane is not pure diffusion, for the ratio between the exchanging water and salt (the *diffusion-volumes*) should then remain constant.

On the other hand, the approximation to uniformity favours the idea of the existence of a numerical relation between the osmose and diffusate. So also may the circumstance be considered, that sugar and sulphate of magnesia, which approximate as seen above in their osmose, were found before to have a similar degree of diffusibility*. The facts appear to afford a strong presumption, but no demonstrative proof, of the intervention of diffusion in governing the results of osmose in such neutral substances. The influence of diffusion becomes more difficult to trace in the osmose of three other neutral salts, which I shall now introduce. What has been represented as the chemical agency now begins to interfere more sensibly, although not to govern the results entirely as it appears to do in less strictly neutral salts.

Chloride of Sodium.—The osmose of chloride of sodium possesses a certain interest independently of such theoretical considerations.

* Philosophical Transactions, 1850, p. 10.

TABLE VII.—Chloride of Sodium in Osmometer C of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Chloride of sodium.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				days.	min.	°
0·25	12	0·552	.....	2	16	63
0·25	8	0·368	0·068	1	16	63
1	3	0·138	0·230	1	6	66
1	13	0·598	0·242	1	8	66
2	11	0·506	0·506	1	6	67
2	16	0·736	0·511	1	3	69
5	46	2·34	1·513	2	3	72
5	51	2·30	1·468	1	2	70
10	78	3·496	2·994	1	15	67
10	82	3·60	2·648	1	2	67
20	165	7·36	6·645	1	2	67
20	167	7·452	6·190	1	2	67

Chloride of sodium is known to diffuse with nearly double the rapidity of sulphate of magnesia in the smaller proportions of salt, and with a still higher velocity in the larger proportions of salt; accordingly the diffusates in the last Table exceed those of sulphate of magnesia in a corresponding ratio. The osmose appears pretty uniform, but with a tendency to fall below the average rate of the salt in the low proportions, such as 1 and 2 per cent., and to exceed the same rate in the higher proportions of salt. In a septum of single membrane, the osmose of a 10 per cent. solution was observed to rise to a high amount.

TABLE VIII.—Chloride of Sodium in Osmometer H of single membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				day.	min.	°
2	21	1·04	0·917	1	16	66
2	24	1·20	0·955	1	16	68
10	272	13·28	6·502	1	16	68
10	311	15·68	7·850	1	12	68

An observation was made on the osmose of a high proportion of salt with another single membrane, differing from the last in offering considerably less hydrostatic resistance.

TABLE IX.—Chloride of Sodium in Osmometer I of single membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				days.	min.	°
10	198	8·692	3·968	3	2·5	68
10	194	8·528	5·297	1	2·5	68

To these I add a series of observations of the osmose of the same salt in albumen, with the view of exhibiting the phenomenon in septa of that material. The well-preserved proportionality of the diffusate is remarkable.

TABLE X.—Chloride of Sodium in Osmometer K of albuminated calico for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				days.	min.	°
1	16	.....	0·141	4	8	65
1	27	.....	0·219	1	8	62
4	39	.....	.....	1	2	60
4	34	.....	0·625	3	2	56
10	43	.....	1·580	1	3	59
10	61	.....	1·615	1	3	60
10	72	.....	1·597	1	3	61
1	27	.....	0·153	1	2·5	63
1	22	.....	0·141	2	4	63
0·1	27	.....	0·016	1	2·5	63
0·1	29	.....	0·018	1	4	64

Chloride of Barium.—Chloride of barium in its rate of diffusion from open vessels much resembles the chloride of sodium. Considerable analogy between the same salts is also observed in osmotic experiments.

TABLE XI.—Chloride of Barium in Osmometer L of double membrane for five hours.

I. Salt in solution.	II. Rise in millimeter degrees.	III. Same in grammes of water.	IV. Diffusate in grammes.	V. Previous maceration.	VI. Hydrostatic resistance.	VII. Temperature, FAHR.
per cent.				days.	min.	
2	35	1·476	.....	2	10	72°
2	45	1·886	0·675	1	10	70
5	94	3·936	1·706	1	8	67
5	111	4·674	1·640	1	6	67
5	74	3·116	1·203	1	10	67
10	154	6·478	4·491	1	10	67
10	133	5·576	3·395	10	16	64
10	136	5·74	2·929	1	4	64
20	267	11·214	6·860	1	8	68
20	283	11·79	7·030	1	8	65
1	60	2·542	0·275	1	8	65
1	74	3·116	0·230	1	8	64
5	74	3·116	0·602	2	8	66
5	74	3·116	1·587	1	8	67
10	152	6·396	3·795	2	8	67
10	154	6·478	4·040	1	8	69
20	337	14·186	.....	1	8	70
20	320	13·448	8·130	1	8	70

Chloride of Calcium.—The diffusion of chloride of calcium in open vessels has been observed to fall below that of chloride of barium as 7·5 to 6·5*. But in membrane, judging from the following observations, the diffusion of chloride of calcium is the more rapid of the two. The osmose has also a tendency to rise, particularly in the larger proportions of chloride of calcium. The replacing water often exceeds twice the weight of the salt diffused.

TABLE XII.—Chloride of Calcium in Osmometer M of double membrane for five hours.

I. Salt in solution.	II. Rise in millimeter degrees.	III. Same in grammes of water.	IV. Diffusate in grammes.	V. Previous maceration.	VI. Hydrostatic resistance.	VII. Temperature, FAHR.
per cent.				days.	min.	
2	6	0·258	.....	2	8	72°
2	6	0·258	0·795	1	8	70
5	45	1·935	2·29	1	8	67
5	60	2·64	1·83	1	3	67
5	51	2·24	2·636	1	8	67
10	228	9·92	4·256	1	8	67
10	188	8·24	3·607	10	12	64
10	176	7·76	3·11	1	6	64
20	389	17·2	6·075	1	3	68
20	398	17·6	.....	1	3	65
2	24	1·04	0·668	1	4	65
2	27	1·2	0·625	1	4	64
5	81	3·6	1·512	2	5	66
5	83	3·68	1·467	1	5	67
10	185	8·16	3·158	2	5	67
10	181	8	3·317	1	5	69
20	406	18	6·695	1	5	70
20	416	18·4	6·992	1	5	70

* Philosophical Transactions, 1850, pages 817 and 819.

These three chlorides, possessing about double the diffusibility of sugar and sulphate of magnesia, should be replaced by half as much water as the latter substances. Some approach to this ratio may be perceived amid much irregularity in the observed osmose of the chlorides.

Proceeding now to the salts in which the osmose appearing to depend upon chemical properties preponderates greatly over osmose from diffusion, I may introduce these substances under the metals which they contain for the sake of their relations in composition.

Potassium and Sodium.

Hydrate of Potash.—A highly intense osmose appears to be determined by caustic alkali, but it is necessary to apply the smallest proportions of alkali to avoid the rapid dissolution of the membrane. In double membrane 0·01 per cent. of hydrate of potash, or 1 alkali in 10,000 water, gave an osmose of 81 and 58 ms. By four times as much alkali, or 0·025 per cent., an osmose of 49 and 67 ms. was produced. These are the greatest effects.

On increasing the proportion of hydrate of potash to 0·5 per cent. the osmose sunk to 22 and 26 ms.; with 1 per cent. of hydrate of potash to 13 ms. The permeability to hydrostatic pressure was always very great, being never less than one drop in a minute.

By the action of the alkali in the last experiment the permeability was increased from three to nine drops, and the membrane entirely ruined.

A similar experiment with hydrate of potash was made in albuminated calico with similar osmotic results. In the 0·01 per cent. solution an osmose of 76 and 58 ms. was observed; in 0·025 per cent. solution 87 and 126 ms.; in 0·5 per cent. solution 15 and 12 ms., and in 1 per cent. solution — 10 ms., or a small negative osmose. The permeability both before and after the last experiment was represented by one drop in one minute; in both the half per cent. experiments the permeability was one drop in three minutes; in the preceding 0·025 per cent. solutions one drop in $2\frac{1}{2}$ minutes, and at the beginning one drop in ten and five minutes with the 0·01 per cent. solutions. The alkali first became sensible to the test-paper in the water-jar, in the diffusion of the 0·025 per cent. solutions. During both series of experiments the temperature ranged from 58° to 62°.

Carbonate of Potash.—The high osmose of this salt has already been often referred to in illustration of the influence of alkaline salts. The following experiments may be compared with those upon the neutral substances lately discussed, particularly in regard to their diffusates. They show also the comparative influence of membrane applied single and double to an osmometer.

Table XIII.—Carbonate of Potash in Osmometer B of single membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Proportion of salt.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				day.	min.	
2	635	28·576	0·514	1	20	66
2	695	31·236	0·548	1	20	68
10	892	40·128	2·897	1	16	68
10	900	40·508	3·045	1	16	68

The fluid was removed from the water-jar at the expiration of the third hour, and replaced by distilled water to prevent the reaction of that portion of the salt which had already reached the jar upon the progress of diffusion from the osmometer, both in the preceding and the following series of experiments.

Table XIV.—Carbonate of Potash in Osmometer D of double membrane for five hours.

Proportion of salt.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				day.	min.	
2	449	21·883	0·324	1	16	66
2	484	23·621	0·400	1	16	68
10	619	30·178	2·764	1	16	68
10	595	28·993	3·150	1	12	68

In the double membrane, the average osmose of the 2 per cent. solution is reduced to 466 ms., from 665 ms. in the single membrane. The change is similar in the 10 per cent. solution, namely a reduction to 607 from 896 ms.; a reduction of nearly one-third of the osmose in the double membrane for both proportions of salt.

The difference of the diffusates is much less marked; for they may be said to be the same for the 10 per cent. solutions, namely 2·966 grammes in the single, and 2·957 grammes in the double membrane; and for the 2 per cent. solution 0·531 gramme in the single, and 0·326 gramme in the double membrane. The diffusion of carbonate of potash, as seen here in membrane, will be found to correspond well with that of chloride of sodium (Table VII.), as the diffusion of the same two salts in open vessels is known to present a near approach to equality. The great osmose or current of fluid inwards might be supposed to diminish the outward movement of the salt under diffusion by washing back the salt into the osmometer. But the diffusates of the 10 per cent. solutions appear to have suffered no remarkable reduction from that or any other cause. The diffusate of carbonate of potash, which usually passes through membrane, appears, however, to be low. In the 1 per cent. solution, formerly referred to (page 188), it was 0·195 gramme. In the series of observations, likewise already

referred to (page 187), the diffusate of carbonate was also low but remarkably uniform, namely 0·018 gramme for 0·1 per cent. solution, 0·092 gramme for 0·5 per cent. solution, and 0·196 gramme for the 1 per cent. solution.

But these determinations were all made by the alkalimetrical method, and when in subsequent observations the potash was also determined by weighing it as sulphate, the proportion of diffusate was found sensibly increased. It hence appears that carbonate of potash acts chemically upon the membrane, and that a portion of the alkali diffuses out in a neutralized state. Thus in five successive experiments with the 1 per cent. solution, in fresh double membrane, the diffusates by the alkalimetrical method were 0·208, 0·254, 0·264, 0·215 and 0·189 gramme carbonate of potash; while the actual quantity of alkali found by direct analysis corresponded in the last four observations to 0·318, 0·353, 0·287, and 0·242 gramme. The quantity of carbonate of potash which has suffered change in passing through the membrane is 0·064, 0·089, 0·072 and 0·053 gramme in these four experiments respectively.

The diffusates of carbonate of potash, increased by those quantities, approach too closely to those of chloride of sodium to warrant the supposition of any peculiar repression by membrane of the diffusion of carbonate of potash, which otherwise appeared probable.

The observations last commented upon belong to a number undertaken with the view of ascertaining three points of interest, which may excuse a fuller statement of the experiments. These points were, first, the influence upon osmose of the air dissolved in solutions of carbonate of potash, which might be supposed to take a part in the chemical action of the membrane; secondly, the effect of frequent repetition of the experiment in exhausting the osmotic activity of membrane; and, thirdly, the relation in osmose of an alkaline carbonate and phosphate.

TABLE XV.—Solutions in Osmometer L of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Temperature, FAHR.
Carbonate of potash, 1 per cent.	439	63
Same, deprived of air by boiling	376	64
Same, deprived of air by boiling	353	65
Same solution, unboiled	325	63
Same solution, unboiled	268	56
Phosphate of soda ($2NaO\,HO\,PO_5$) 1 per cent.	176	55
Same	194	58
Same, 0·1 per cent.	196	56
Same, 0·1 per cent.	190	58
Carbonate of potash, 0·1 per cent.	176	57
Same, 0·1 per cent.	227	65
Same, 1 per cent.	298	58
Same, 1 per cent.	335	64
Same, 1 per cent.	312	62

It will be remarked that the highest osmose (439 ms.) is obtained in the first expe-

riment, and that the osmose falls off pretty regularly to the fifth experiment (268 ms.). The change in the aëration of the solution in the second and third experiments cannot be said to interfere with this progression. The influence of free oxygen on the membrane is not therefore indicated as a cause of osmose. It may be added, that the converse experiment of depriving the fluid of the water-jar of air by boiling, led also to a negative result. It will be remembered, further, that the osmose of oxalic acid was not interfered with by an addition of sulphurous acid, which was likely to counteract the action of oxygen, if such an action existed in osmose.

When phosphate of soda is substituted for carbonate of potash, both 1 per cent., the osmose declines from 268 to 176 ms. The phosphate of soda being repeated, the osmose rises a little, namely to 194 ms. The one-tenth per cent. solution of the same salt which follows, maintains here the considerable osmose of 196 and 190 ms. On returning again to the application of carbonate of potash in the instrument, the osmose gradually rises and regains 335 ms. for the 1 per cent. solution of that salt.

From these repetitions of osmose it may be inferred, that whatever be the nature of the chemical action on membrane which prompts osmose, that action is by no means of a rapidly exhaustible character.

It may be added, with regard to the osmotic action of extremely dilute solutions of carbonate of potash, that the osmose is lowered rapidly in proportions below one-tenth of a per cent. of that salt. The osmose of 0·01 per cent. of carbonate of potash, in double membrane, amounted only to 19, 23 and 17 ms. in three successive experiments. The osmotic action of carbonate of potash must, therefore, be inferior to that of hydrate of potash in the extreme degrees of dilution.

In the experiments of the preceding series, the influence of a salt often appears not to terminate with its presence in the osmometer, but to extend to following experiments made with other salts, or made with different proportions of the original salt. If this arises from portions of the first salt remaining in the membrane, they must be portions which are not easily washed out. The substance of membrane may possibly have an attraction for highly osmotic salts, capable of withdrawing small quantities from solution. When the membrane, however, is removed from the osmometer, after such experiments as are referred to, slightly washed and then incinerated, only minute traces of the salt last used are commonly discovered; if indeed the salt has not entirely disappeared.

Phosphate and Carbonate of Soda.—The osmose of the carbonate of soda appears to be quite similar to that of carbonate of potash. A considerable amount of information respecting the two soda salts named is conveyed in the following series of experiments, which includes also observations on the serum of ox-blood.

TABLE XVI.—Solutions in Osmometer F of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Temperature, FAHR.
		°
Phosphate of soda, 1 per cent.	382	63
Same, 1 per cent.	311	56
Same, 0·1 per cent.	205	55
Same, 0·1 per cent.	218	58
Carbonate of soda, 0·1 per cent.	294	56
Same, 0·1 per cent.	254	58
Same, 0·01 per cent.	50	57
Same, 0·01 per cent.	39	65
Same, 1 per cent.	306	58
Same, 1 per cent.	337	64
Phosphate of soda, 1 per cent.	193	62
Same, 1 per cent.	186	61
Serum of ox-blood, undiluted	39	59
Same	34	61
Same, diluted with equal vol. of water	31	61

The phosphate and carbonate of soda, when alternated in the same osmometer, show considerable steadiness in their respective rates of osmose.

The inferior osmotic quality of serum is remarkable, considering the alkalinity of that fluid. The loss of osmose in serum is due, I believe, to the presence of chloride of sodium. The latter substance possesses an extraordinary power of reducing the osmose of alkaline salts, which was observed in a variety of circumstances, but which it will be sufficient to illustrate by the following series of experiments in an albumen osmometer.

TABLE XVII.—Solutions in Osmometer N of albuminated calico for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Diffusate in grammes by analysis.	Same, by alkalimetry.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
				days.	min.	°
Carbonate of soda, 1 per cent.	139	0·157	0·092	1	3	57
Same, 1 per cent.	150	0·156	0·106	1	6	59
Same, 2 per cent.	141	.....	0·242	1	6	65
Same, 4 per cent.	143	0·570	.....	1	8	62
Same, 10 per cent.	204	1·562	1·450	1	12	60
Same, 10 per cent.	163	1·432	1·340	3	6	56
Same, 1 per cent.	138	0·216	0·147	1	6	59
Same, 1 per cent.	136	0·198	0·156	1	3	60
Same, 0·1 per cent.	188	.....	0·005	1	10	61
Same, 0·1 per cent.	179	.....	.....	1	6	63
Carbonate of soda 0·1 per cent. + chloride of soda 1 per cent.	32	.....	.....	2	6	63
Same + same	36	.....	.....	1	6	63
Chloride of sodium, 1 per cent.	25	0·384	.....	1	6	64
Same, 1 per cent.	18	0·325	.....	1	3	65
Carbonate of soda 1 per cent. + chloride of soda 1 per cent.	69	.....	.....	1	5	63
Same + same	56	.....	.....	3	8	56
Carbonate of soda, 1 per cent.	157	0·190	0·164	1	6	55
Same, 1 per cent.	163	0·212	0·185	1	4	58
Same, 0·1 per cent.	152	.....	.....	1	20	56
Same, 0·1 per cent.	152	.....	.....	1	20	58

The osmose of the 0·1 per cent. solution of carbonate of soda is lowered by the addition of 1 per cent. chloride of sodium, from 179 ms. to 32 ms. The osmose of 1 per cent. carbonate of soda, with the addition of an equal proportion of chloride of sodium, is 56 ms., and of 1 per cent. carbonate of soda alone, immediately following, 157 ms. The osmose of these mixtures appears to be assimilated to that of chloride of sodium itself, which comes out as 18 and 25 ms. in the same series of observations.

The rise of an alkaline liquid in the osmometer appears to be equally repressed by chloride of sodium, placed outside or dissolved in the fluid of the water-jar.

In illustration of this statement, I may adduce a short series of observations made with fresh ox-bladder, having its thickness unreduced, which further show that the repressing power that appears in the chloride of sodium does not extend to two other substances, alcohol and sugar.

TABLE XVIII.—Solutions in Osmometer P of ox-bladder for five hours.

Salt in osmometer.	Rise in millimeter degrees.
Carbonate of potash, 0·25 per cent.	76
Same, 0·25 per cent.	96
Carbonate of potash, 1 per cent., against alcohol, 1 per cent., in jar	108
Same, 1 per cent., against sugar, 1 per cent., in jar	104
Same, 1 per cent., against chloride of sodium, 1 per cent., in jar	18
Same, 1 per cent., against pure water in jar	114
Same, 1 per cent., against chloride of sodium, 1 per cent., in jar	18
Carbonate of potash, 1 per cent.+chloride of sodium, 1 per cent., against water in jar	64
Carbonate of potash, 1 per cent., alone, against pure water in jar	134
Same repeated	114

Now another neutral salt, sulphate of potash, will be found to have the reverse effect upon the osmose of an alkaline carbonate, supporting and promoting the latter. Such results show how far we still are from a clear comprehension of the agencies at work in membranous osmose. Another property of chloride of sodium, equally singular, is, that the association of this salt (by itself so indifferent) with small proportions of hydrochloric acid, such as one-tenth per cent., determines a positive osmose in membrane, which is sometimes very considerable.

The osmotic action of the albuminated calico of Table XVII. is moderate in amount, but remarkably uniform. The small tenth per cent. solution assumes a pre-eminence in activity which is very curious. It was often observed in the inquiry, that the small proportions of active salts were more favoured in albuminated calico than in membrane; may it not thence be inferred that it is in the albumen plate that the chemical agency operates to most advantage?

Taking the mean diffusates of chloride of sodium and carbonate of soda from the lower part of the same Table, we have 0·354 chloride of sodium against 0·201 carbonate of soda, or 1 of the former to 0·568 of the latter. The diffusates of the

same two salts, in open vessels, were more nearly in the proportion of 1 to 0·7. The comparative diffusion of carbonate of soda appears to be rather repressed than promoted by the septum.

The neutralization of a portion of the alkaline salt during the osmotic process is again indicated. The portion of carbonate of soda thus lost in the 1 per cent. solution appears to diminish on repetition of the experiment. At the head of the table, the loss in two experiments is 0·065 and 0·050 gramme; lower down, 0·069 and 0·042 gramme; and near the bottom of the table, 0·026 and 0·027 gramme. The loss with the 10 per cent. solution is 0·110 and 0·092 gramme, or not more than double the loss in the preceding 1 per cent. solutions of carbonate of soda.

Sulphates of Potash and Soda.—The sulphate of potash was made the subject of frequent experiment, with the view of obtaining light on the nature of osmose, at the commencement of the inquiry. But it is not well fitted for such a purpose, its action in the osmometer proving at first of a most perplexing character. With thick ox-bladder, sulphate of potash dissolved in the proportion of 1 per cent., usually exhibited considerable osmose, that is, about one-half of the osmose of carbonate of potash in similar circumstances. The osmose of the sulphate had, however, a peculiar disposition to increase in successive repetitions of the experiment with the same membrane. The osmose of this salt might also be doubled by allowing bladder in substance to macerate for some time in the solution before the osmotic experiment; soluble matter from the membrane manifestly influenced the result considerably in all experiments with sulphate of potash.

When the removal was effected of the muscular coat of bladder, the chief source of its soluble matter, the osmose of the salt in question fell greatly in amount instead of rising, like that of the carbonate of potash.

In the prepared membrane sulphate of potash presented a small moderate osmose, like chloride of sodium. But the salt must be exactly neutral to test-paper, and the membrane also free from foreign saline matter, otherwise very different results are obtained. In a double membrane, 1 per cent. of the neutral sulphate gave 21 and 20 ms.; but the same solution, made alkaline by the addition of no more than one ten-thousandth part (0·01 per cent.) of carbonate of potash, started up to 101 and 167 ms., a much greater osmose than the proportion of carbonate of potash present gave afterwards by itself in the same membrane, namely 19, 23, and 17 ms. The influence of the alkali is so persistent, that the membrane, macerated in water for a night after the last experiments, still gave 65 ms. with 1 per cent. of pure sulphate of potash.

The osmotic activity of sulphate of soda is equally excited by a trace of alkali, and both sulphates exhibit the same character in albumen as well as in membrane. This remarkable result of the combined action of the two salts is so likely to elucidate the chemical actions prevailing in osmose, that a fuller series of illustrative experiments may be recorded. The septum was of double calico, well albuminated, and presented a good resistance to hydrostatic pressure.

TABLE XIX.—Solutions in Osmometer Q of albuminated calico for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Temperature, FAHR.
		°
Sulphate of potash, 1 per cent.	18	53
Same	21	57
Sulphate of potash, 1 per cent. + carbonate of potash, 0·01 per cent.	139	62
Same + same	81	56
Same + same	73	61
Same + carbonate of potash, 0·1 per cent.	254	61
Same + same	263	59
Carbonate of potash, 0·1 per cent., alone	92	57
Carbonate of potash, 0·1 per cent., alone	95	57
Sulphate of soda, 1 per cent. + carbonate of potash, 0·1 per cent.	257	62
Same + same	237	54
Same + carbonate of soda, 0·1 per cent.	299	54
Carbonate of soda, 0·1 per cent., alone	90	57
Same	127	58

The influence of the two alkaline carbonates in giving a high osmose to the sulphates, appears to be pretty nearly equal. The primary source of the great osmose may prove to be the action on membrane of the alkaline carbonates, which is promoted in some way by the presence of sulphate of potash, as it is retarded by the presence of chloride of sodium.

On the other hand, the moderate amount of osmose which appears to be proper to these sulphates is completely negatived by the most minute addition of a strong acid. Thus, 1 per cent. of sulphate of potash, with the addition of one ten-thousandth part (0·01 per cent.) of hydrochloric acid, had its osmose reduced, in the first experiment to 8 ms., and in the second experiment to −5 ms., the osmose becoming actually negative.

On one occasion, a specimen of well-crystallized sulphate of potash gave, when dissolved, a still more sensible negative osmose, namely −28 ms. On applying litmus to the solution, it was found to possess an acid reaction. But the addition of 0·01 per cent. carbonate of potash was sufficient to change the acid into an alkaline reaction, and to give rise to a positive osmose, amounting to 54 ms.

It occurred to me to macerate a fresh membrane in water, containing one-thousandth part (0·1 per cent.) of hydrochloric acid, for two days, before applying the membrane to the osmometer, and then to wash the membrane with distilled water till all acid reaction disappeared. With 1 per cent. of neutral sulphate of potash, this membrane gave in succession 17, 42, 35 and 62 ms.; with sulphate of soda, 1 per cent., following, 39, 25 and 25 ms.; and with sulphate of zinc (anhydrous), 1 per cent., after the last salt, 14 and 21 ms. These last results show a certain degree of unsteadiness in the osmose of the alkaline sulphates, probably arising from the osmose of these salts depending so much upon adventitious circumstances. The diffusates were carefully weighed, first when fully dried, at 212°, and again when ignited. The difference in

the weighings arose from the presence of organic matter dissolved out of the membrane, of which it gives the quantity probably somewhat exaggerated.

First diffusate, 0·328 grm. sulphate of potash.
Second diffusate, 0·362 grm. sulphate of potash, 0·019 grm. organic matter.
Third diffusate, 0·351 grm. sulphate of potash, 0·031 grm. organic matter.
Fourth diffusate, 0·366 grm. sulphate of potash, 0·025 grm. organic matter.
Fifth diffusate, 0·356 grm. sulphate of soda, 0·011 grm. organic matter.
Sixth diffusate, 0·339 grm. sulphate of soda, 0·019 grm. organic matter.
Seventh diffusate, 0·334 grm. sulphate of soda, 0·009 grm. organic matter.
Eighth diffusate, 0·239 grm. sulphate of zinc.
Ninth diffusate, 0·260 grm. sulphate of zinc.

The diffusates of the two alkaline sulphates are remarkably uniform, the diffusate of sulphate of soda falling a little under that of sulphate of potash, but not so much as in open vessels. The diffusate of sulphate of zinc is still smaller but relatively too high, as it should not much exceed one-half of that of sulphate of potash, judging from the diffusion of these salts in the absence of membrane. The organic matter accompanying the salt falls off in quantity in successive experiments, but continued to exist to the last, although it was not determined in the experiments with sulphate of zinc. The diameter of the disc of membrane was 123 millimeters, and its original weight, air-dried, 0·559 gramme.

Oxalate of Potash, Chromate and Bichromate of Potash.—The only property of sulphate of potash which seems to be connected with the positive osmose of that salt, is its bibasicity as a sulphate. The alkaline character promotes positive osmose, and this character appears to be a distinction of polybasic salts. The common tribasic phosphate of soda is strongly alkaline to test-paper, and the bibasic pyrophosphate of soda enjoys the same property in a still higher degree. The sulphates of potash and soda are certainly neutral to test-paper, but they may be looked upon as potentially alkaline from the easy severation of the second equivalent of fixed base and its replacement by water, witnessed in all bibasic salts. In monobasic salts, on the contrary, a proclivity to the acid character may be suspected. Thus although the chloride of potassium and nitrate of potash appear as neutral to test-paper as the sulphate of potash is, yet the chlorides and nitrates of the magnesian bases are more decidedly acid than their sulphates. It is just possible then on this view, that the osmotic inferiority of chloride of sodium, and the power of that salt to counteract the positive osmose of carbonate of potash, may be exhibitions of acid character belonging to the former salt. The observations of the rise in the osmometer of chloride of sodium, and also of the chlorides of barium and calcium, previously described, also have the appearance of being the effect of diffusion, modified by a slight chemical osmose of a negative character proper to these salts.

The polybasic constitution of oxalate of potash is well marked, and its positive

osmose will be found below to be considerable, although the specimen of salt employed was strictly neutral to test-paper.

This salt also, like sulphate of potash, is shown not to counteract the high positive osmose of an alkaline carbonate.

The chromate of potash, although carefully purified by crystallization, retained a slight alkaline reaction. On this account small additions were made to it of bichromate of potash in some experiments, but without materially diminishing the very sensible positive osmose of the former salt. A neutral chromate has of course the same bibasic character as a sulphate.

TABLE XX.—Oxalate and Chromate of Potash in Osmometer F of double membrane for five hours.

Solution of salt.	Rise in millimeter degrees.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
			days.	min.	°
1 per cent. oxalate of potash	164	.....	1	11	65
Same	153	.....	1	10	65
0·1 per cent. oxalate of potash	92	.....	1	5	63
Same	90	.....	2	6	61
1 per cent. oxalate of potash + 0·1 per cent. carbonate of potash	262	.....	8	5	56
Same + same	337	.....	1	5	60
0·1 per cent. carbonate of potash	322	.....	1	3	62
Same	273	.....	1	3	68
1 per cent. oxalate of potash + 0·1 per cent. carbonate of potash	294	.....	1	3	62
Same + same	246	.....	2	3	55
1 per cent. bichromate of potash	24	0·253	1	3	54
Same	19	0·318	2	1	56
1 per cent. chromate of potash	109	0·326	1	1	62
Same	106	0·307	1	1	58
1 per cent. chromate of potash + 0·1 bichromate of potash	91	0·298	2	1	57
Same	79	0·281	1	1	60

The average rise for the 1 per cent. solution of each of the salts placed in the osmometer in a pure state is, bichromate of potash 21·5 ms., chromate of potash 107·5 ms., and oxalate of potash 158·5 ms. The average diffusate for the chromate of potash is 0·3165 gramme, and for the bichromate of potash 0·2855 gramme.

Like solutions were submitted to osmose at the same time in a septum of albumen for the sake of comparison with the preceding membrane osmometer.

Table XXI.—Oxalate and Chromates of Potash in Osmometer K of albuminated calico.

Solution of salt.	Rise in millimeter degrees.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
			days.	min.	°
1 per cent. oxalate of potash	195	.....	1	15	65
Same	173	.....	1	15	65
0·1 per cent. oxalate of potash	91	.....	1	15	63
Same	100	.....	2	20	60
1 per cent. oxalate of potash + 0·1 per cent. carbonate of potash	161	.....	8	15	56
Same + same	211	.....	1	15	60
0·1 per cent. carbonate of potash	109	.....	1	15	62
Same	120	.....	1	15	68
1 per cent. oxalate of potash + 0·1 per cent. carbonate of potash	195	.....	1	15	62
Same + same	188	.....	2	15	55
1 per cent. bichromate of potash	36	0·244	1	15	54
Same	34	.....	2	10	56
1 per cent. chromate of potash	129	0·253	1	10	62
Same	123	0·242	1	10	58
1 per cent. chromate of potash + 0·1 per cent. bichromate of potash	95	0·251	2	10	57
Same	102	0·320	1	10	60

The average rise for the 1 per cent. solution of each of the salts is, for bichromate of potash 35 ms., for chromate of potash 126 ms., and for oxalate of potash 184 ms., all a little higher than in the previous membrane osmometer. The diffusate is lower than before, probably owing to the less permeability of the albuminous septum, the weight of chromate of potash diffused being 0·2475 gramme, and of bichromate of potash 0·244 gramme.

The two chromates have been found to possess nearly equal diffusibility in open vessels, and to correspond closely in that property with sulphate of potash. The oxalate of potash exhibits a considerable osmose when present in the small proportion of one-thousandth part (0·1 per cent.), namely 91 ms. in membrane and 95·5 ms. in albumen. This is the surest indication of considerable osmotic capacity. Bin-oxalate of potash and free oxalic acid are both remarkable for high negative osmose.

Barium, Strontium, Calcium, Magnesium.—The salts of these metals never appear capable of producing strong positive osmose when dissolved in a proportion of less than 1 per cent. On the contrary, some of the salts of this class, particularly the nitrates, exhibit a tendency to negative osmose.

Hydrate of Baryta gave a small positive osmose for minute proportions of salt, which disappeared as the proportion of salt was increased, exhibiting an analogy in this respect to hydrate of potash. The results for hydrate of baryta in double membrane were 6, 4, 1 and 1 degrees of osmose for the 0·1, 0·25 and 0·5 per cent. solutions. In albumen the same solutions gave 0, −8, −23 and −17 ms.; and the 1 per cent. solution gave −25 ms.

Hydrate of Lime exhibited similar characters to the last base. Undiluted lime-water gave in double membrane —20 ms. and —1 m.; while the same, diluted with four volumes of water, gave a positive osmose of 31 and 18 ms. In albumen the undiluted lime-water gave —48 and —30 ms.; the same, diluted with four volumes of water, gave 0 m. and 1 m.

Chloride of Strontium, 1 per cent., gave in double membrane 19, 27 and 26 ms., following chloride of barium in the same membrane, 13 and 21 ms. Nitrate of baryta, in the same membrane, gave 12, 24 and 29 ms.; nitrate of strontia, following the latter, 27 and 31 ms.

Nitrate of Lime in membrane twice gave 19 ms., following chloride of calcium with 12 and 20 ms.; in albumen nitrate of lime gave 2 and 2 ms.

The two per cent. solution of the same salt in membrane gave only 6 and 6 ms. in two experiments.

Chloride of Magnesium gave in membrane —2 ms. and in albumen 6 ms., both experiments being made with the one per cent. solution, which is always to be understood when no particular per-centage is stated.

Nitrate of Magnesia gave in membrane —24 and — 20 ms. Both of these magnesian salts were prepared by saturating the acid with excess of magnesia. The tendency of monobasic salts of the magnesian class to chemical osmose of a negative character appears to be small in the salts of barium and strontium, to rise in those of calcium, and to culminate in the salts of magnesium itself.

Aluminium.—Nothing is more remarkable than the high positive osmose of certain salts of alumina. These salts emulate the alkaline carbonates in this respect. The property too appears to be characteristic of the sesquioxide type, and distinguishes the salts of sesquioxide of iron, sesquioxide of chromium and the higher oxide of uranium, as well as alumina.

Sulphate of Alumina.—The sulphates of this type do not exhibit a high degree of osmose, although they are probably more osmotic than the magnesian sulphates as a class. Sulphate of alumina, 1 per cent., gave in membrane 57 and 67 ms., and for 0·1 per cent. 24 and 31 ms.

The diffusate was small, amounting in the second observation of the 1 per cent. solution to 0·033 gramme of tersulphate of alumina, together with an excess of 0·005 grm. of sulphuric acid, according to analysis.

Chloride of Aluminium, prepared by treating hydrochloric acid with an excess of hydrated alumina, was found by analysis to approach very nearly to the proportions of the definite compound Al_2Cl_3. The following results with that salt were successively obtained in an osmometer of single membrane:—

With 1 per cent., rise of 540 ms. at 50° Fahr.
With 1 per cent., rise of 570 ms. at 49° „
With 1 per cent., rise of 450 ms. at 47° „
With 1 per cent., rise of 635 ms. at 49° „

With 0·1 per cent., rise of 510 ms. at 54° Fahr.
With 0·1 per cent., rise of 285 ms. at 48° „
With 0·1 per cent., rise of 410 ms. at 56° „

The numbers, which are all high, vary considerably among themselves, as often happens when osmose is intense and is observed in a single membrane. The temperatures of the water-jar are added in these and most other observations recorded, although it was difficult to draw any positive conclusion respecting the influence of heat upon the osmose of small proportions of salt. With large proportions of neutral salts, where diffusibility prevails, the osmose appeared to increase with the temperature, as does the proportion of salt diffused. With respect to the condition of the membrane used above, the first experiment was conducted in the membrane freshly dissected and previous to any maceration or washing whatever, with a similar osmotic result, it will be observed, as in the later experiments made with the membrane after being repeatedly macerated.

In experiments of diffusing chloride of aluminium in open vessels, decomposition of that salt was observed with escape of free hydrochloric acid. The decomposition appeared however to affect much less of the chloride of aluminium than it does of the acetate of alumina.

In an albumen osmometer, chloride of aluminium gave an osmose of 245, 233 and 229 ms., at 57°, 58° and 60°, with diffusates of 0·085, 0·123 and 0·095 gramme of salt, calculated from the quantity of chlorine found in the diffusate.

In the last experiment the solution was coloured with litmus, apparently without affecting the amount of osmose.

Acetate of Alumina was prepared by precipitating pure sulphate of alumina by means of the acetate of lead. Mr. Crum has shown that in this reaction one equivalent of acetic acid becomes free, and that the acetate of alumina produced has the form $Al_2O_3+2C_4H_3O_3$. A specimen of the pure binacetate, prepared by Mr. Crum, exhibited an equally high osmose as the salt mixed with free acid obtained by precipitation, which is used below.

Table XXII.—Acetate of Alumina in Osmometer G of double membrane for five hours.

Proportion of salt.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	
1	232	9·728	.....	2	3·5	65
1	264	11·096	.....	1	3·5	65
0·1	195	8·208	.....	1	3·5	64
0·1	130	5·472	0·036	2	3	66
0·1	159	6·688	0·051	1	3	67
0·1	146	6·152	0·045	2	3	67

In the second and third experiments of the Table, the solutions were coloured distinctly blue, by means of the ordinary sulphate of indigo, without interfering much apparently with the osmose.

The diffusates, when given, are as binacetate of alumina, and were calculated from the alumina found in the water-jar.

In the last three observations of the one-tenth per cent. solution, the diffusate of salt is in proportion to the replacing water as 1 to 152, 131 and 137.

In osmometer F of single membrane, acetate of alumina gave a diffusate not exceeding one-third or one-fourth of the diffusate from sulphate of potash in similar circumstances. Thus, in three observations of the aluminous salt, the osmose was 356, 393 and 397 ms., with the corresponding diffusates of 0·102, 0·114 and 0·080 gramme of binacetate of alumina; while two experiments on sulphate of potash, which were intercalated between the second and third of the preceding observations, gave diffusates of 0·325 and 0·425 gramme of sulphate of potash.

The osmose of acetate of alumina does not appear to be sensibly affected by previous experiments made in the same membrane with sulphuric acid, but to fall greatly when an equal proportion of sulphate of potash is diffused along with the acetate of alumina. Of the following numbers, —4, 8, 7, 237, 7 and 18, the first three and the fifth, which are small, are the osmose of 0·1 per cent. sulphuric acid alone; the fourth, which is large, that of 1 per cent. of acetate of alumina, and the sixth that of 1 per cent. of acetate of alumina mixed with 1 per cent. of sulphate of potash, all in the same membrane. The diffusate of the pure acetate of alumina was 0·087 gramme, which is low for a 1 per cent. solution, as compared with the diffusates from the one-tenth per cent. solutions of sulphuric acid, which were 0·039, 0·042, 0·046 and 0·044 gramme of sulphuric acid.

The addition of an equal weight of chloride of sodium to the one per cent. solution of acetate of alumina, lowered the osmose of the latter salt, in osmometer F, from 397 to 267 ms. This is a small amount of interference compared with that exercised by the sulphate of potash in the same membrane.

Pure binacetate of alumina was found to be largely decomposed when diffused in open vessels, the acetic acid escaping and leaving behind the allotropic soluble alumina of Mr. Crum. This last substance is remarkable for its low diffusibility, but this subject will require further discussion on a future occasion.

Iron.—Protosulphate of Iron. This salt appeared, like sulphate of magnesia, to exhibit only the exchange by diffusion of one part of salt for five or six parts of water; the rise of fluid in the osmometer also increasing pretty uniformly with the proportion of salt. Thus, in double membrane of good resistance, 1 per cent. of this salt (always supposed anhydrous) gave 21 and 30 ms.; 4 per cent. 60 and 84 ms., at a temperature between 61° and 64° Fahr.

Protochloride of Iron.—This salt separates itself from some other magnesian chlorides, and gives rise to a positive chemical osmose, which is considerable in amount.

To learn whether this arose from the passage of iron into the higher oxide or not, sulphurous acid and hydrosulphuric acid were mixed with the protochloride of iron, but, as will be seen below, without lessening the osmose.

TABLE XXIII.—One per cent. Solutions of several Magnesian Chlorides in Osmometer F of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Hydrostatic resistance.	Temperature, FAHR.
		min.	°
Chloride of magnesium	3	2	59
Chloride of zinc	48	2	61
Same	54	2	62
Chloride of manganese	24	1·75	62
Same	34	1·5	63
Protochloride of iron	160	1	61
Same	197	1	64
Same	435	2	65
Protochloride of iron + 0·1 per cent. sulphurous acid	404	4	62
Protochloride of iron saturated with SH	332	4	64
Protochloride of iron, alone	155	4	61

The osmose of protochloride of iron is large, but singularly unsteady in amount, rising from 160 to 435 ms., and falling again to 155 ms.

In another double membrane, of rather small resistance (1 min.), the osmose of the same salt was only 94, 91 and 97 ms. Between the first and second of these experiments the membrane was washed with alcohol and ether, but without changing the character of the osmose. In experiments made with this last membrane, the 2 per cent. solution of protochloride of iron gave 151 and 157 ms.; and the 5 per cent. solution 189 ms., or the osmose did not rise in proportion to the quantity of salt in solution.

Nitrate of Sesquioxide of Iron, formed by saturating dilute nitric acid by hydrated sesquioxide of iron, gave, in single membrane, the high osmose of 322 and 359 ms. for one per cent. of salt; and 153, followed by 107 ms., for 0·1 per cent. of salt. The acetate of the same oxide gave, when of a deep red colour, 207 ms., and when it had become nearly colourless, from the spontaneous precipitation of a portion of its oxide, 194 ms., or sensibly the same osmose.

Manganese.—Sulphate of manganese appeared to have no decided chemical osmose, giving in double membrane of moderate resistance (2 min.), for 1 per cent. of salt, 34, 51 and 50 ms.; for 4 per cent. of salt, 53 and 51 ms., and for 10 per cent. of salt, 57 and 59 ms. The low osmose of the larger proportions of this salt is exceptional and would require confirmation.

The chloride of manganese has already been shown to be of low osmose in membrane (24 and 34 ms. Table XXIII.); in albumen the same salt gave 13 and 14 ms.

Cobalt.—The chloride of this metal appeared to possess no decided chemical

osmose, 1 per cent. giving in double membrane 21 and 27 ms.; 0·1 per cent. 20 and 23 ms., and 1 per cent. again 44 ms.

Nickel.—The sulphate of oxide of nickel resembled that of magnesia and protoxide of iron. In double membrane 1 per cent. gave 12 and 10 ms.; 4 per cent. 38 and 38 ms.; 10 per cent. 72 and 106 ms.

The chloride of nickel, however, appeared to have a tendency to chemical osmose, like the protochloride of iron, and gave in double membrane 52, 89 and 95 ms.

Zinc.—None of the salts of this metal can be said to exhibit decided chemical osmose; sulphate of zinc giving 34 and 29 ms., nitrate of zinc 18 and 32 ms., and chloride of zinc 48 and 54 ms., all in double membrane.

Cadmium.—The nitrate of cadmium appeared to affect chemical osmose; the one per cent. solution of this salt giving, in double membrane, 90, 124 and 137 ms.

Copper.—Copper appears to possess the capacity for chemical osmose in its salts generally, with the exception of the sulphate. But no sulphate appears to be remarkable for osmotic activity. The comparative osmose of four salts of copper in the same membrane is given below.

TABLE XXIV.—Solutions of 1 per cent. of Salts of Copper in Osmometer E of double membrane for five hours.

Salt in solution.	Rise in millimeter degrees.	Hydrostatic resistance.	Temperature, FAHR.
		min.	°
Chloride of copper.....	351	1	60
Sulphate of copper.....	48	10	59
Nitrate of copper	154	10	60
Same	204	12	62
Acetate of copper	148	10	62
Same	102	10	63
Same	101	10	61

The rate of osmose is generally a little deranged on passing from one salt to another in the same membrane, and in consequence the second or third experiment is always to be preferred to the first made with the same salt. The preferable numbers for the osmose of the preceding salts would therefore be, sulphate of copper 48 ms., acetate 102, nitrate 204, and chloride 351. The number for the sulphate, however, is probably too high, being raised by the previous chloride.

The salts of several of the magnesian metals exhibit a much lower osmose in albumen than in membrane. In an osmometer of the first description nitrate of copper gave only 22 and 27 ms.; acetate of copper 22 and 25 ms., or no more osmose than is obtained from the corresponding salts of lime and magnesia.

Lead.—The salts of this metal are probably equally osmotic with those of copper. The nitrate and acetate of lead only were examined. The osmose of these two salts obtained in the same membrane was as follows:—

TABLE XXV.—Solutions of 1 per cent. of Salts of Lead in Osmometer M of double membrane for five hours.

Salt in solution.	Rise in millimeter degrees.	Hydrostatic resistance.	Temperature, FAHR.
		min.	°
Nitrate of lead	174	2	64
Same	211	2	65
Same	197	2	62
Acetate of lead	100	2	64
Same	97	2	61

The numbers which these results appear to authorize, were for acetate of lead 97 ms., and for nitrate of lead 204 ms. (mean of 211 and 197 ms.). The acetate exhibits, as usual, a considerably inferior osmose to the nitrate of the same base.

It appeared desirable to ascertain the osmose of higher proportions of a salt, which, like the nitrate of lead, exhibits decided osmose in the 1 per cent. solution. The first results appearing low, the membrane was washed with ether after the third experiment, a treatment of the membrane which in this instance sensibly improved its osmotic power.

TABLE XXVI.—Solutions of Nitrate of Lead in Osmometer K of double membrane for five hours.

Proportion of salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.					min.	°
1	91	.....	.....	0	2	61
1	127	.....	.....	1	1	64
1	125	.....	.....	1	1	63
1	157	.....	.....	3	8	63
1	157	.....	.....	9	12	63
2	184	.....	.....	1	12	63
2	195	.....	.....	1	12	66
5	209	.....	.....	1	12	66
5	229	.....	.....	1	12	67
10	213	.....	.....	1	12	69
10	250	10·56	3·283	2	16	72

These experiments lead to the estimation of the osmose of nitrate of lead as follows:—in the 1 per cent. solution an osmose of 157 ms., in the 2 per cent. solution 195 ms., in the 5 per cent. solution 229 ms., and in the 10 per cent. solution 250 ms. This, it is to be observed, is but a small increase for the higher proportions of salt. The diffusate for the 10 per cent. solution of this salt may be considered of an average proportional amount. The replacing water then exceeds the salt diffused only about three and a half times.

It is curious that the hydrostatic resistance of the membrane increases so decidedly as the experiments advance, in the osmose of this and several other metallic salts,

particularly nitrates. It is not to be supposed, however, that this change has any material influence upon the osmose.

Uranium.—The nitrate of uranium presented a high degree of osmose. This result scarcely affects the question of the constitution of the metallic oxide present in that salt, as a high osmose is exhibited, both by the salts containing an oxide of the type $R_2 O_3$, and by a portion at least of the class of protoxides. Viewed as an aluminous salt the nitrate of uranium has a basic composition ($Ur_2 O_3 NO_5$), a circumstance which suggested the addition of free nitric acid to that salt in some experiments. The small proportion of one-tenth per cent. of nitric acid will be seen to have a moderate influence, and 1 per cent. of nitric acid to have an overpowering influence in reducing the extraordinary osmose of this salt.

TABLE XXVII.—Solutions of Nitrate of Uranium in Osmometer M of double membrane for five hours.

Proportion of salt in solution.	Rise in millimeter degrees.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
			days.	min.	°
1 per cent. nitrate of uranium	288	0·078	1	1	60
1 per cent. nitrate of uranium	458	0·102	3	1	61
Same + 1 per cent. nitric acid	44	0·205	1	1	63
Same + same	70	0·136	1	3	66
Same + 0·1 per cent. nitric acid	304	0·078	1	3	62
Same + same	282	0·108	1	3	61

The inferior osmose of the first observation in the Table arose from the osmose of the early hours of the experiment being less than those of the later hours, the osmose for the five hours in succession being 36, 46, 67, 77 and 63 ms.

This progression, combined with the additional circumstance to be observed, that the diffusate is below the average in the same experiment, suggests the idea of an absorbing or retaining power in the membrane for the salt, which must first be satisfied before the osmose and diffusion can proceed in a regular manner.

The diffusate is throughout small, like that of an aluminous salt.

In an albumen osmometer the osmose of the same salt was inconsiderable, namely 49 and 53 ms.; but that osmose was not further reduced by the addition of nitric acid.

Tin.—The protochloride of tin exhibits a high degree of osmose, like so many other metallic protochlorides. The one per cent. solution gave, in double membrane, an osmose of 235, 253, 289 and 275 ms. The bichloride of tin following immediately in the same membrane gave only 27 ms. But the osmose of the bichloride of this metal is essentially negative, even when the salt is made as neutral in composition as possible. It has been already described (page 192).

Antimony.—The double tartrate of potash and antimony proved rather remarkable for low osmose.

In the first experiment with a double membrane the osmose of the salt in question was 38 ms., but the osmose fell in the second and third repetitions to 12 and 17 ms. The 4 per cent. solution of the same salt gave no more than 23 and 7 ms.

Mercury.—The osmose of the salts of both oxides of this metal is always positive and generally considerable. The osmose appeared to be of least amount in the chloride (corrosive sublimate), to increase in the protonitrate, and to assume its greatest magnitude in the pernitrate. The first salt has a stability in solution which the latter two salts do not enjoy.

Extraordinary osmose is here, therefore, associated with facility of decomposition, as in so many other instances.

The influence of the presence of acids and of chloride of sodium upon the osmose of chloride of mercury was tried in the search for facts which might throw light on the osmotic process.

An acid in small proportion appears to favour, rather than otherwise, the osmose of chloride of mercury. Chloride of sodium, on the other hand, exerts its usual repressing influence upon the process.

TABLE XXVIII.—Solutions of Mercury in Osmometer C of double membrane for five hours.

Proportion of salt in solution.	Rise in millimeter degrees.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
		days.	min.	°
1 per cent. of chloride of mercury	116	4	4	60
Same	121	3	4	61
0·1 per cent. of chloride of mercury	62	1	4	63
Same	49	1	5	66
1 per cent. of chloride of mercury + 0·1 per cent. of hydrochloric acid	163	1	5	62
Same + same	132	1	4	61
Same + 0·1 per cent. of nitric acid	152	3	5	60
Same + same	122	1	2	59
Same + 0·5 per cent. of chloride of sodium...	72	1	2	61
Same + same	60	1	1	62

Adopting the second experiments as the most trustworthy, we have for 1 per cent. of chloride of mercury an osmose of 121 ms., and for the same, associated with half its weight of chloride of sodium, 60 ms.

The osmose of chloride of mercury in albumen was very trifling, being only 5 and 9 ms.; chloride of mercury diffused in sensible quantity, however, through both the albumen and membrane.

Protonitrate of mercury gave, in double membrane, an osmose of 232, 346 and 350 ms.; in albumen, much less, namely 47, 63 and 61 ms.

Pernitrate of mercury gave, in double membrane, 425 and 476 ms. for the one per cent. solution, and 296 ms. for the one-tenth per cent. solution, results which indicate osmotic power of the highest intensity.

The membrane preserved a considerable action after the last experiments, although macerated in water for a night, and imparted thereafter to a salt nearly neutral to osmose (nitrate of silver), a rise of 222 and 166 ms.

In albumen, pernitrate of mercury again was low, giving 32 and 54 ms. for one per cent. of the salt, and 34 and 46 ms. for the one-tenth per cent. solution.

Silver.—It is interesting to observe how this metal separates itself from mercury and the magnesian elements, and takes its place with the alkaline metals in the property of osmose, as in other chemical characters. Nitrate of silver appeared to possess a moderate positive osmose, like a salt of potash or soda. For the sake of comparison, the silver salt was followed by nitrate of soda in the experiments below.

TABLE XXIX.—Solutions in Osmometer G of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
		days.	min.	°
1 per cent. of nitrate of silver	36	1	2	64
Same	34	1	2	65
0·1 per cent. of nitrate of silver	27	1	2	62
Same	22	1	2	64
1 per cent. of nitrate of soda.....	7	2	2	61
Same	2	1	2	64

The experiments of the Table indicate an average osmose of 35 ms. for 1 per cent. of nitrate of silver, and of 4·5 ms. for the same proportion of nitrate of soda. A considerable diffusate of silver appeared in all the experiments with the salt of that metal.

Gold and Platinum.—The chlorides of these metals have already been shown to possess a decided negative osmose, and in that respect to rank with acids.

In concluding this paper, I may place together a series of numerical results which exhibit the osmose of substances of all classes. Some of these numbers have not been previously reported.

Osmose in membrane of 1 *per cent. solutions expressed in millimeter degrees.*

Oxalic acid	−148	Chloride of zinc	45
Hydrochloric acid (0·1 per cent.)	− 92	Chloride of nickel	88
Terchloride of gold	− 54	Nitrate of lead	204
Bichloride of tin	− 46	Nitrate of cadmium	137
Bichloride of platinum	− 30	Nitrate of uranium	458
Nitrate of magnesia	− 22	Nitrate of copper	204
Chloride of magnesium	− 2	Chloride of copper	351
Chloride of sodium	+ 12	Protochloride of tin	289
Chloride of potassium	18	Protochloride of iron	435
Nitrate of soda	14	Chloride of mercury	121
Nitrate of silver	34	Protonitrate of mercury	350
Sulphate of potash	21 to 60	Pernitrate of mercury	476
Sulphate of magnesia	14	Acetate of sesquioxide of iron	194
Chloride of calcium	20	Acetate of alumina	393
Chloride of barium	21	Chloride of aluminium	540
Chloride of strontium	26	Phosphate of soda	311
Chloride of cobalt	26	Carbonate of potash	439
Chloride of manganese	34		

It will be observed that acid and alkaline salts are found at opposite ends of the series, or, while the acids possess negative osmose, the alkaline salts exhibit positive osmose in the highest degree. The remark will suggest itself, that in osmose water always appears to pass to the alkaline side of the membrane; as water also follows hydrogen and the alkali in electrical endosmose.

The chemical action must be different on the substance of the membrane at its inner and outer surfaces to induce osmose; and according to the hypothetical view, which accords best with the phenomena, the action on the two sides is not unequal in degree only, but also different in kind. It appears as an alkaline action on the albuminous substance of the membrane at the inner surface, and as an acid action on the same substance at the outer surface. The most general empirical conclusion that can be drawn is, that the water always accumulates on the alkaline or basic side of the membrane.

The analogy does not fail even when the osmometer is charged with an acid solution and the osmose is negative. The stream is then outwards to the water, which is a basic body compared with the acid within the membrane.

The high positive osmose of the salts of the alumina type is exceedingly remarkable. The property is common to salts of alumina, sesquioxide of iron, sesquioxide of chromium, and the corresponding oxide of uranium. Now the property in these salts is small where the salt is stable, as in the sulphates, but becomes great where the affinity between the acid and base is comparatively weak, as in the chlorides, nitrates and acetates of these bases, salts which can be shown to be largely decomposed in the

experiment by the action of diffusion. When pernitrate of iron, a salt of this class, is placed in the osmometer, a rapid decomposition of the salt occurs in the membrane; the nitric acid escaping, from its high diffusibility, into the water of the jar, and leaving a basic salt on the inner surface of the membrane. Here then, as with the preceding class of osmotic bodies, the osmose of the water is towards the basic side of the membrane.

But the most curious circumstance, with reference to this empirical generalization, is observed in the magnesian class of salts. The barytic subdivision of this class, including all the soluble salts of baryta, strontia and lime, appear to be entirely unosmotic, or they oscillate between a small positive and small negative osmose. Such salts are neutral in their reaction, and further, have no disposition whatever to form subsalts. The salts of the earth, magnesia itself, offer the same characters. But in the salts of certain other oxides of the magnesian group an intensely osmotic character is developed, particularly in the salts of copper, protoxide of lead and protoxide of tin, with the exception of the soluble sulphates of these bases. Now those named are the members of the magnesian class most apt to break up into free acid and a basic salt. Like the aluminous salts, therefore, they are capable of investing the inner surface of the membrane with basicity, the necessary condition of positive osmose. Nitrate of uranium does not require to form a subsalt, as it is already constitutionally basic. The osmotic peculiarity of metaphosphoric acid, formerly referred to, also harmonizes with the same view.

Neutral monobasic salts of the alkaline metals, such as the chlorides of potassium and sodium and the nitrates of potash, soda and silver, which possess a strict and unalterable neutrality, appear to have little or no true osmotic action. The salts named, together with the neutral magnesian sulphates and certain neutral organic substances, such as alcohol and sugar, give occasion, it is true, to an increase in the fluid of the osmometer, but only to the moderate extent which the exchange of diffusion-volumes might be supposed to produce. The comparative diffusibility of all these substances is well known, with the exception, unfortunately, of that of water itself, which I could only deduce by an indirect method in my previous inquiries respecting liquid diffusion. As salts generally appeared to diffuse in water four times more rapidly than they did in alcohol, the diffusibility of water was then assumed as probably four times greater than that of alcohol, and consequently five or six times greater than that of sugar or sulphate of magnesia. Diffusion is thus made to account for the substances last named being replaced in the osmometer by five or six times their weight of water. This "diffusion-osmose" appears to follow in its amount the proportion of salt in solution, with a certain degree of regularity. The "chemical osmose" of substances, on the other hand, is found of high intensity with small quantities of the substance, such as 1 per cent. or even 0·1 per cent., and to augment very slowly with increased proportions of the substance in solution.

A small proportion of common salt accompanying carbonate of potash has been

seen to possess a singular influence in diminishing the positive osmose of the last-named alkaline salt; while a mixture of small proportions of common salt and hydrochloric acid exhibits, with the membrane in certain conditions, an intense positive osmose which neither of these substances possess individually.

The bibasic salts of potash again, such as the sulphate and oxalate, although strictly neutral in reaction, begin to exhibit a positive osmotic power, in consequence, it may be supposed, of their resolvability into an acid salt and free alkaline base.

The sulphate of potash, when strictly neutral, has in different membranes a variable but always moderate positive osmose, an osmose which the slightest trace of a strong acid may cause to disappear entirely, or even convert into a small negative osmose.

On the other hand, a minute addition of an alkaline carbonate to the sulphate of potash appears to give that salt a positive osmose of a high order. It was seen that the mixed salts produce much more osmose than the sum of the osmose of the two salts used apart from each other.

This property of sulphate of potash must wait for its explanation, with many other facts of the subject, till fuller information is obtained than I can at present offer respecting the nature of the obscure chemical changes which occur in the membrane during osmose, and of the mode in which masses of water come to participate in these changes. The conclusion which has been drawn, that the osmose or movement of water through membrane is always towards the side of the base, is no theory or explanation of the phenomenon, but a general description, which appears to apply with sufficient accuracy to all the observations.

It may appear to some that the chemical character which has been assigned to osmose takes away from the physiological interest of the subject, in so far as the decomposition of the membrane may appear to be incompatible with vital conditions, and osmotic movement confined therefore to dead matter. But such apprehensions are, it is believed, groundless, or at all events premature. All parts of living structures are allowed to be in a state of incessant change,—of decomposition and renewal. The decomposition occurring in a living membrane, while effecting osmotic propulsion, may possibly therefore be of a reparable kind. In other respects chemical osmose appears to be an agency particularly well adapted to take part in the animal œconomy. It is seen that osmose is peculiarly excited by dilute saline solutions, such as the animal juices really are, and that the alkaline or acid property which these fluids always possess is another most favourable condition for their action on membrane. The natural excitation of osmose in the substance of the membranes or cell-walls dividing such fluids seems therefore almost inevitable.

In osmose there is, further, a remarkably direct substitution of one of the great forces of nature by its equivalent in another force—the conversion, as it may be said, of chemical affinity into mechanical power. Now, what is more wanted in the theory of animal functions than a mechanism for obtaining motive power from chemical decomposition as it occurs in the tissues? In minute microscopic cells the osmotic

movements should attain the highest velocity, being entirely dependent upon extent of surface. May it not be hoped, therefore, to find in the osmotic injection of fluids the deficient link which intervenes between chemical decomposition and muscular movement?

The intervention of the osmotic force is also to be looked for in the ascent of the sap of plants. The osmometer of albuminated calico appears to typify the vegetable cell; the ligneous matter of the latter being the support of a film or septum of albuminous matter, in which the active properties of the cell reside. With a vegetable salt, like oxalate of potash above, and pure water below such a septum, an upward movement of the lower fluid would necessarily ensue.

VIII. *Researches on the Impregnation of the Ovum in the Amphibia; and on the Early Stages of Development of the Embryo. (Third Series.)* By the late George Newport, *F.R.S., F.L.S. &c. Selected and arranged from the Author's MSS.*, by* George Viner Ellis, *Professor of Anatomy in University College, London. Communicated by Sir* John Forbes, *M.D., F.R.S.*

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In a note dated April 18th, 1853, which was added to my last paper on the "Impregnation of the Ovum†," whilst it was printing, I recorded the fact that, "through the adoption of a different mode of examination" from that which I had previously employed, I had seen the spermatozoon pass through the gelatinous covering and the vitelline membrane of the egg into the vitelline chamber and the yelk. This fact of the penetration of the spermatozoon into the yelk is of such importance as to make it necessary for me to state, with precision, all the circumstances connected with it, and to detail the exact course I have pursued. These particulars were not given when I announced the fact, because they would have exceeded the limits of a supplementary note; but as the omission of them has exposed my statement to considerable doubt on the part of one of the most distinguished and truthful of physiologists (Professor Bischoff‡), it is the more necessary that I now detail precisely my mode of proceeding§. I think it will then appear, that the difficulties which have hitherto prevented a solution of the question of the penetration of the egg of the Frog by the spermatozoon are in chief part, if not entirely overcome, and that this egg, far from being the least fitted, is perhaps one of those best adapted for arriving

[* A great part of this paper was written by Mr. Newport, with the intention of presenting it to this Society; and the rest has been compiled from his *Note Books*. None of the observations were made later than the Spring of 1853.—G.V.E.]

† Philosophical Transactions for 1853, p. 271.

‡ In a paper purporting to refute the opinions of Dr. Keber and Dr. Nelson concerning the penetration of the spermatozoon into the ovum, "Widerlegung, &c. &c., von Dr. Th. L. W. Bischoff, mit einem Zusatz von Dr. Rud. Leuckart."

[§ Since the above sentence was written Professor Bischoff has investigated, this spring (1854), the impregnation of the egg of the Frog, and has confirmed the statement of Mr. Newport respecting the penetration of the spermatozoon. See his pamphlet headed "Bestätigung des von Dr. Newport bei den Batrachien und Dr. Barry bei den Kaninchen behaupteten Eindringens der Spermatozoiden in das Ei." In this publication he asserts that Mr. Newport is the discoverer of the phenomenon of the *penetration of the spermatozoon into the egg by its own movement*.—G.V.E.]

at the settlement of the dispute about penetration, which has so long engaged the attention of physiologists.

Mode of proceeding.

I have elsewhere mentioned that I employed a glass cell to contain the egg whilst it was examined*, with the view of keeping it in one position, and preventing the movement derived from accidental causes: it is made of a section of a piece of barometer tube, from one-eighth to one-fourth of an inch deep and three lines in diameter in the clear, which is cemented on a plate of glass of convenient size. This piece of apparatus, which I name a *tube-cell*, is of a size sufficient to contain only a single egg after its covering is fully expanded. For the purpose of making an observation, the egg is to be placed in the centre of the cell, immediately after removal from the body of the frog, and before it has come into contact with any fluid; by this proceeding the gelatinous envelopes adhere so firmly to the glass as to render the egg almost or quite immoveable, when the jelly expands on the subsequent addition of water. In order that the proper focal distance of high magnifying powers may be obtained, I commonly use a cell which allows the object-glass to be immersed in the fluid.

As this cell admits light on every side, it is well adapted for viewing the penetration of the spermatozoon into the egg envelopes when the microscope is placed vertically, and a strong transmitted light is employed. It is convenient also for viewing the egg laterally with a simple plano-convex lens of low power, with the view of observing the formation of the chamber above the yelk, or watching the cleavage of the yelk; but the experience of some years has proved that the cell is not suited for the lateral examination of the egg with the compound microscope, owing to the thickness and the convexity of its wall. True, the passing of the spermatozoon into the external envelope, and even *into* the vitelline membrane, can be readily observed when the tube cell is employed in the upright position of the microscope, but I have been unable to follow satisfactorily the course of the spermatozoon completely *through* the yelk membrane in that position of the object, in consequence of the dark colour and opacity of the egg.

To ascertain the fact of the impregnation of the ovum by penetration, it was then necessary to invent some means by which the egg could be examined laterally with the compound microscope. The great difficulty to be overcome was the tendency of the dark surface of the fecundated ovum to maintain a vertical position, with the consequent rotation or rather gravitation of the whole mass of the yelk, whenever there was any change in the position of the cell. I contrived for this purpose a cell or box larger than the one before described, which may be designated a *cistern box*; and with it I could note all the changes that took place whilst the egg was quite undisturbed. This box resembles the animalcule cage of Mr. Tully†, since it is

* Philosophical Transactions for 1853, p. 267.

† A Practical Treatise on the Microscope, by John Quekett, p. 130, 2nd edit.

constructed of brass with glass at the top and bottom, and it is inserted into a brass plate by which it may be fixed to the stage of the microscope: the front glass can be approximated to or removed from the hinder one by means of the sliding of the piece of brass in which it is cemented, though this motion never allows the glasses to touch. The glass employed is thin, especially the front one; and a piece is cut out of the anterior one (about one-third of the whole) to allow of water being added or removed by a siphon without disturbing the box or its contents. Its diameter is eight-tenths to nine-tenths of an inch, and its least depth is about one-sixth of an inch, or about sufficient for the lodgment of a single row of the frog's eggs, before they are expanded. During the use of this box the microscope is placed horizontally; and a camera is attached to the eyepiece to allow of the immediate delineation of the changes seen.

The magnifying power used has been commonly the half-inch object-glass (Ross) with No. 2 eyepiece, but when any doubt has arisen the quarter-inch object-glass has been taken; and the illumination has been derived from the apparatus called GILLET's condenser.

If the following points are attended to, the entrance of the spermatic body may be readily seen. The eggs are to be passed uninjured from the frog*, and are to be attached immediately to the inner surface of the glass plate in the moveable front of the cistern box; the front of the box is to be replaced and the objects brought into focus, and then the box is to be filled with spermatozoic water. As soon as the fluid touches the eggs, these imbibe it and expand, but they remain firmly attached to the glass. In order that the success of the experiment may be ensured, equal parts of the sperm and water may be used, and within a few minutes after the former has been obtained; this will cause a large number of spermatozoa to enter the egg; but as the mixture is too opake for the satisfactory observation of the phenomena, I remove it at the end of two or three minutes by means of a siphon, and supply its place with pure water. By this time many of the sperm bodies have begun to enter the ovum, and their transit to the vitelline chamber is facilitated by the endosmose of the water.

When these circumstances have been attended to, spermatozoa may be sometimes seen at the *zona pellucida* of the envelope within the first minute, though only those that encounter the egg at right angles; but in from four to five minutes many may be visible, according to the number contained in the water. After the lapse of some time, varying with the temperature, the formation of the *chamber* may be noticed over the centre of the dark surface of the yelk: it is usually at this stage, and for a short time afterwards, that the spermatozoa are first detected in, or passing into, the vitelline chamber.

Penetration of the Spermatozoon into the Yelk.

The fact of the penetration was first observed on the 25th of March, 1853, not

* Philosophical Transactions for 1851, p. 188.

only into the chamber, but also into the substance of the yelk; and as soon as I was satisfied of it, the following precise observations were made.

First set of observations.—An observation was begun at 11^h 28^m A.M. with the temperature 60° FAHR. of the room, though possibly it was three or four degrees higher to the eggs, from the radiation of the lamp.

Within five minutes an abundance of spermatozoa could be observed sticking in the vitelline membrane.

At twelve minutes the number was greatly increased, and extended around all the circumference of the membrane within focus: some were still in motion, and passing slowly on through the gelatinous envelope with their characteristic serpentine movement.

At seventeen minutes the number of the spermatozoa sticking in the vitelline membrane appeared to be lessened.

At twenty-two minutes the yelk had changed its position, the dark part being uppermost; and I could distinctly see some spermatozoa sunk in the vitelline membrane and shining through it, as in former observations, but I could not yet detect any within the cavity of the yelk: some of the bodies, both those in the yelk membrane and those in the jelly, were perishing, as the curling up of the tails showed.

In thirty minutes the yelk had begun to separate from its envelope (forming the *chamber*), and in the small space thus forming at the middle of its upper surface, I saw two spermatozoa in motion.

At thirty-seven minutes the space was increased and more spermatozoa were in it.

At 1^h 4^m the bodies were still moving, though the greater number were folded up both in the chamber and on the yelk, but some had their tails projecting out of the yelk membrane; the chamber had attained to half of its future dimensions.

At 1^h 22^m all motion had ceased, and there was a heaving of the yelk. From this period till segmentation began, the spermatozoa in the chamber became gradually fainter, till they appeared to change into fine elementary granules, and then disappeared; but some of those that entered the dark surface of the yelk remained for more than twenty minutes after its first cleavage, whilst others that were sticking in the vitelline membrane were perceptible for many hours.

In the glass box were three other eggs, in all of which the same facts could be noted. The segmentation of the yelk began at the end of three hours and thirty minutes at the temperature stated. I may mention, that in each egg two spherical bodies, to be presently described, were present, and that these exist in all perfectly or imperfectly fecundated eggs.

The observations were repeated on the evening of the same day on a set of four eggs; and were repeated on the three following days with precisely similar results.

Second set of observations.—I now proposed to vary the conditions of the eggs by having a temperature of the room of 64° FAHR., there being the corresponding

increase from the lamp, and by using pure sperm that had been obtained an hour before.

At $12^h\ 50^m$ a single egg was immersed in undiluted male fluid.

At twenty-two minutes after immersion I saw spermatozoa passing through the vitelline membrane at all points of its surface, whilst some had passed through it. The yelk was beginning to separate from its membrane, and its surface had an undulatory motion. As the chamber enlarged, several spermatozoa became evident within it in motion.

At $1^h\ 45^m$ several of the spermatozoa were fast disappearing, as if breaking up into granules, but those outside the membrane did not disappear so rapidly as those within the chamber.

Some other eggs, four in number, were experimented on with some of the same fluid used for the egg referred to above, and in this case the fluid had been removed from the male for two hours and a quarter; the fluid remained on the eggs half an hour, and its place was then supplied by pure water. Temperature 64° Fahr. as before.

At thirty minutes, that is to say, as soon as the water was added, the chamber was in three eggs largely developed, as much as it would have been in an hour in eggs only moderately supplied with spermatozoa, though in the fourth egg the degree was not quite so great. From eight to twelve spermatozoa were detected in each chamber, and some motionless in the fluid; others on the vitelline membrane had their serpentine movements; and others were projecting from the membrane motionless, as if their force had been expended before they could effect an entrance.

This last experiment seems to favour my view, that the changes in the yelk are hastened by excess of the fecundating fluid.

From the facts stated above, and before detailed in my former papers, the conclusion seems to be arrived at, that the fructifying of the egg depends on the force or power residing in the sperm body to make its way through the thick coverings of the yelk; and that, this being the case, an explanation will be afforded of the failure of the fluid to occasion fecundation when those bodies are deficient in number or well-being, or are deprived of the power of moving: and at the same time the penetrating power may afford a clue to the inability of filtering paper, even when it is twice or thrice folded, to stop their progress through it.

The action of the spermatozoon is influenced by the temperature of the air, and by mechanical impediments to its passage into the egg.

With respect to temperature, I have frequently referred to its influence in expediting or retarding the development of the embryo, and the following general statement may be given in support of it. A given number of eggs, at a mean temperature of 61° Fahr., will advance in *four* days as far as a corresponding set, at a mean temperature of only 47° Fahr., will reach in fourteen days. Further, the embryos exposed to the low temperature mentioned above die and decompose, whilst

in a running stream, and in a natural state, they would come to maturity, and this difference appears to be owing to the more perfect aëration of the water in the natural than in the artificial development.

There is a certain condition of the envelopes of the egg, of not very unfrequent occurrence, which affects the impregnation. In this condition the envelope is semi-opake and thickened, and the alteration is induced I suspect by too long retention of the ova in the oviduct during a period of excitement: this pathological state seems interesting, as it may have its representative in the ova of other animals, and may be operative in like manner in them.

On the 15th of March, 1853, I employed in an experiment a pair of frogs that had been in constant union since their capture eight days before, and on passing the eggs in the usual way I noticed (what I had before observed) that the envelope was more opake or clouded, thicker and more irregular than usually. On fecundating the eggs with recent healthy sperm I found the changes were slower in their occurrence, and the number of embryos formed was much smaller than in experiments on eggs with healthy envelopes. Thus out of fifteen eggs in separate cells, not more than a third were fecundated; and in these, at a temperature of 60° Fahr., the chamber could not be perceived with a lens till after the lapse of an hour and ten minutes, instead of less than an hour; and segmentation of the yelk did not begin for three hours and fifty-five minutes at a temperature of 60° to 65° Fahr., instead of at about three hours and twenty minutes.

The results were still more marked in two other sets of eggs, fifty in each, where a smaller quantity of spermatozoa was employed, and more time occupied in making the experiments; for in the one set, only three or four eggs were segmented with but one embryo; and in the other set, a very few underwent segmentation, and but three embryos were afterwards produced.

These and other experiments show that the unusual condition of the egg affected the process of fecundation, and that to this cause the failure in the production of embryos is to be attributed. And as the act of fecundation is accomplished through the motor power or force of the spermatozoon, by which that body is enabled to pass through the coverings of the healthy egg, it appears that, when there is any deficiency in the usual power, arising from an unhealthy condition of the fertilizing body, or an increase in the resistance in the yelk coverings, the spermatozoon is unable to pass through the membranes into the yelk, and the egg remains unfertilized.

Of the spherical bodies which appear on the Yelk after fecundation.

I have already alluded* to the presence of certain spherical bodies, which appear within the clear chamber of the egg of the Frog, and on the surface of the yelk subsequent to fecundation. Like bodies have been noticed, especially in the Gasteropodous Mollusca, among the Invertebrata, and have been even seen in some of the

* Philosophical Transactions, 1851.

Mammalia, but their evolution has not hitherto been traced, nor their signification been understood*.

I may now detail the results of an experiment carefully made for the purpose of ascertaining somewhat of their origin and destination; this one will serve as a type of all.

On the 27th of March 1853, and at a temperature of 61° FAHR., three eggs were put in a cell and impregnated in the usual way.

* A single spherical body, projected from the surface of the yelk and maintained for a period at a distance from it on a pedicle, was first noticed in *Lymnæus stagnalis* by CARUS in 1824 (Von der äusseren Lebensbedingungen der weiss- und kaltblütigen Thiere, p. 33. t. i. fig. 4), before the investigations of BAER and PURKINJE had directed attention to the structure of the ovum. But this pediculated body was not further regarded by CARUS than as the imagined axis of rotation of the yelk. A similar body, but followed also by a second, was also seen in *Lymnæus* by DUMORTIER in 1837 (Mém. de l'Acad. de Bruxelles, tom. x. p. 136; also Annales des Sciences Naturelles, 2me série, tom. viii. 1837, p. 136), and this was immediately supposed by him to be the analogue of the Purkinjean vesicle, and with its fellow, was believed to give origin to the head and foot of the animal. A single body was also noticed in *Lymnæus* by POUCHET (Sur le développement de l'Embryon des Lymnées, Comptes Rendus, July 1838, pp. 86, 87), and by him likewise was thought to be the Purkinjean vesicle set free from the yelk. But SARS observed two vesicles in *Tritonia*, *Eolis* and *Doris* (WIEGMANN's Archiv, 1837), and VAN BENEDEN found two in *Limax agrestis* (MÜLLER's Archiv, 1841, p. 180) and *Aplysia depilans* (Annales des Sc. Nat. tom. xv. p. 126. pl. 1. figs. 4, 7, 9, 1841), and remarked that in both species these bodies come from the yelk before segmentation is commenced, and that their presence indicates that the body of the *Limax* will be formed on that side of the yelk at which they appear. Nevertheless VAN BENEDEN, observing that they are suspended for a time in the transparent fluid which surrounds the yelk from which they proceed, believed that they become dissolved in this fluid and do not take any direct part in the formation of the embryo; and although he appears to have regarded them as the representatives of the Purkinjean vesicle, he seems to have doubted whether this body plays the important part which has been attributed to it in the higher animals. At the same time he called attention to the fact of the constancy of these vesicles in *Lymnæus*, *Limax* and *Aplysia* as meriting consideration. Yet KARSCH, who afterwards saw the vesicles in *Lymnæus* (WIEGMANN's Arch. xii. 1846, p. 255), thought their presence an abnormal condition. The late Dr. J. REID, however, saw them in *Doris bilamellata* (Annals and Mag. of Nat. Hist. June 1846), and F. MÜLLER in the eggs of *Limapontia* (WIEGMANN's Arch. 1848, p. 1); and although VOGT failed to notice them in *Actæon*, he appears to have seen them in *Limax*, and his remarks (Ann. des Sc. Nat. 3me série, tom. vi. 1846) as to their disappearing in the albumen, coincide with those of VAN BENEDEN.

In the *Nudibranchiata*, NORDMANN appears to have observed at least one of the vesicles in *Tergipes Edwardsii*, although he refers to it as a little vesicle "of air" separated from the yelk (Ann. des Sc. Nat. 3me série, tom. v. 1846, p. 143).

In the *Acephalous Lamellibranchiata* one vesicle at least has been noticed in several genera. It has been remarked by QUATREFAGES in *Teredo navalis* (Ann. des Sc. Nat. 1848), by LOVÉN in *Modiolaria marmorata*, *Cardium pygmæum*, *Patella pellucida*, and *Solen pellucida* (in Kongl. Vetenskaps-Akademiens Förhandl. Decemb. 1848, and MÜLLER's Archiv, 1848, p. 531), and more recently by KEBER in *Unio* and *Anodonta* (De Spermatozoorum introitu in Ovula, Königsberg, 4to, 1853). In *Modiolaria* and *Unio* the vesicle is removed from the yelk on a pedicle, as in Gasteropoda, and this KEBER has miscalled "a *Micropyle*;" while in *Cardium*, *Patella*, *Solen* and *Teredo* the vesicles rest on the surface of the yelk. LOVÉN, who mentions that the germinal vesicle itself disappears in these mollusks before the eggs quit the ovary, has well remarked that the body seen on the surface of the yelk in the fecundated egg before segmentation, cannot therefore be the Purkinjean vesicle itself as supposed by DUMORTIER, and he ingeniously inquires whether it may not be its nucleus.

In the *Annelida*, as in *Mollusca*, one, and in some instances two, vesicles have been seen. KÖLLIKER observed

At thirty-seven minutes the chamber had begun to form, and several moving spermatozoa were in it. The spherical bodies made their appearance on the surface of the yelk; and when first noticed they were closely applied to it, and were surrounded by a small irregular heap of granules. Some of the spermatozoa remained in motion $1^h\ 22^m$, and I have subsequently seen them alive in the chamber for a longer period.

At $1^h\ 30^m$ the two bodies differed somewhat in character, and one was before the other: the anterior or *granulous* one appeared to have a distinct membrane, and to

one in the eggs of *Exogena Œrstedii*, which he at first looked upon as the embryo cell (in Einige Worte zur Entwickelungsgeschichte von *Eunice*. Nachworte von A. Kölliker in Zurich, Nauenberg, 1846, note). Quatrefages also has noticed one in *Hermella* (Ann. des Sciences Nat. 3 série, tom. x. 1848, p. 177. pl. 3. fig. xv. xviii.), and more recently Van Beneden has seen and figured one in the eggs of a Cestoid worm, *Echinebothrium variabile* (Mém. de l'Acad. de Bruxelles, tom. xxv. p. 68, pl. 3. fig. 15. 1850). Thus the existence in many Invertebrata of at least one detached spherical body on the surface of the fecundated yelk, before segmentation, seems to point to the conclusion that these bodies have some important signification with reference to the future embryo. Quatrefages, who has recently directed attention to the fact of their occurrence, properly remarks, that their presence at this stage of development of the egg is much more general than it has hitherto been supposed.

These bodies have been seen equally in the Vertebrata as in the Invertebrata. In the Vertebrata they appear to have been first noticed, but entirely misunderstood, by Dr. Martin Barry in the Rabbit. Although repeatedly seen and figured by him (Philosophical Transactions, 1840, p. 538, Plates XXIV. XXV. and XXVI., figs. 185, 186, 187 and 193, 200, 206, 209, 212), imagining that the germinal vesicle does not disappear before, but only changes its form, becomes enlarged, and takes the place of the yelk, subsequent to fecundation, he conceived that these spherical bodies were the remains of the yelk, or, as he terms it, "*substance*" (p. 538), which he supposed had undergone dissolution and disappeared. Professor Bischoff however, having noticed these bodies in the egg of the Rabbit (Müller's Archiv, 1841, p. 14. tab. 1. fig. 6), directed particular attention to them (Entwickelungsgeschichte des Kaninchen-Eies, 4to. 1842, tab. 2. fig. 17 *b*, figs. 19, 20), and believed them to play an important part in the segmentation of the yelk. Subsequently to this, these spherical bodies were also noticed by Bischoff in the egg of the Dog (Entwickelungsgeschichte des Hunde-Eies, 4to. 1845, tab. 1. figs. 11, 12, 13, 14); and afterwards Pouchet, who had noticed a single vesicle, as before stated, in the Mollusca, gave also *one only* in the egg of the Rabbit, which he has equally regarded as a descendant of the germinal vesicle (Théorie positive de l'Ovulation spontanée et de la Fécondation des Mammifères, Paris, 8vo. 1847, pl. 15. fig. 9). More recently Professor Bischoff has noticed, as in the Rabbit and Dog, two of these spherical bodies in the egg of the Guinea Pig (Entwickelungsgeschichte des Meerschweinchens, 4to. 1852, tab. 1. figs. 5, 6), and I have also found two in the egg of the Frog (Philosophical Transactions, 1853, p. 247). It is thus evident that the appearance of certain spherical bodies on the surface of the yelk, between it and the zona pellucida subsequent to fecundation, and after the yelk has become contracted and ceases to fill the entire zone, and before any subdivision of the yelk is commenced, is a general and perhaps universal occurrence in the fecundated egg both of vertebrated and invertebrated animals, but of the signification of these bodies very different opinions are entertained.

Dr. Bischoff, in his most recent work on the Guinea Pig, states that he formerly believed these bodies to play an important part in the segmentation of the yelk, and that the view he then held has been adopted by Lovén; while F. Müller conceives that these vesicles determine the direction of the segmentation of the yelk. Rathke, on the other hand, regards these vesicles but as accidental occurrences, and of no organic or developmental importance (Erichson's Archives, 1848, p. 187), a view in which he is supported by Desor, in some observations on *Nemertes* (Müller's Archiv, 1848, p. 511), and to which Professor Bischoff himself states he is now somewhat inclined, although he properly remarks that the regularity of the appearance of these vesicles at a definite stage of development of the egg is not favourable to such an opinion (*loc. cit.* p. 19).

be granulated throughout; the other, or *nucleated* body, was clear, and had a distinct granular nucleus on one side. The changes proceeded more rapidly in one of the eggs, but the *bodies* were the same in all.

At $1^h\ 45^m$ the two bodies were passing in a straight line from the centre to the circumference of the chamber. The spermatic particles were fading away and becoming granulous.

At two hours the nucleated one began to change; its nucleus dividing into two granular masses, each of these having a bright spot in its centre. The same change took place in the corresponding body in each egg. Towards the end of the third hour the two masses subdivided, so that four granular masses were present at the centre of the nucleated cell; and in each a bright central spot became very distinct.

The anterior or granular spherical body was still present, and had passed outwards, followed by the nucleated one, to about midway between the central canal and the margin of the chamber above the yelk: the same transference took place in all.

Shortly after the completion of the third hour, it was noticed that the rate of moving towards the margin of the chamber became more rapid, and that the bodies had reached the margin in a direct line with the centre of the yelk surface, one being still at a short distance before the other. When, on viewing the egg laterally, the line of transit corresponds to the line of sight, the change of place is not readily perceived, except the bodies go out of focus; but if their course is at right angles to the line of vision, then the movement is most marked and interesting. When the granular or foremost vesicle has arrived at the margin of the chamber, this space becomes further enlarged by a depression in the centre, marking the commencement of the cleavage of the yelk: granular remnants of the spermatozoa were still recognizable in the chamber.

At $3^h\ 10^m$ the four granular masses in the interior of the nucleated body still cohered together, and seemed to be again subdividing. At this time the little heap of granules, which originally escaped with the spherical bodies from the central canal and remained at its margins, gradually enlarges into a number of small transparent vesicles, in which at first no nuclei are visible: in some of the eggs six or eight of these are to be recognized. In consequence of the transparency of these cells, they are not seen unless the eggs are examined in the way recommended; but during the observation, some attain a third of the size of the spherical bodies. These vesicles usually remain in the vicinity of the central canal from which they came.

About $3^h\ 17^m$ the first division of the yelk is indicated by two clefts which appear at the margins of the canal, and sinking into the substance of the yelk, gradually extend outwards. As the cleft is produced, I have constantly observed the spherical bodies sink into it, and become for a time more or less lost to view; but they do not pass into the substance of the yelk, for they are readily seen in the triangular furrow between the halves, either by means of a reflector above the egg, or when the cleavage lies in the line of vision by the usual mode. When the

cleavage of the egg is at right angles to the line of view the spherical bodies suddenly disappear, and are seen again only when the crucial or second cleft is about to begin.

I may state, that in the eggs under observation, as well as in others examined both before and since, I found, with but very rare exceptions, that both spherical bodies pass together to the same side of the yelk in a line with the entrance of the canal, and one at a little distance behind the other; and that after the completion of the cleavage of the yelk at right angles to the line of sight, the bodies make their appearance again at the spot where they disappeared, and never at any other part of the yelk.

At the end of the fourth hour the first cleft was finished, and the yelk mass contracting at right angles to the cleft, and extending in its direction, the two bodies were again brought into view almost at the very spot at which they disappeared. The same was observed in each egg. This transit, which may be regarded as an indisputable fact, will set aside the opinion that the bodies enter the yelk, and become the foundation of the nuclei of the different parts into which the yelk splits.

It may here be mentioned, with reference to these bodies, that they occasionally are more or less completely detached for a time from the yelk mass during the formation of the chamber. In some instances too, they *appeared* to be absent, as they were not in the usual place, but I found them afterwards adhering temporarily to the inner surface of the vitelline membrane at the point with which they were in approximation at the time of fecundation; in this position they remained till after the first segmentation of the yelk was completed, and then being detached, apparently by the movement of the yelk within its envelope, occupied their usual place in the first furrow. Eggs, with the exceptional condition above described, have always produced embryos; so that whilst we doubt whether the spherical bodies are necessarily connected with the yelk-changes, we see some analogy with the corresponding bodies observed in several of the mollusca, in which they are removed from the yelk during the time it is undergoing the commotion of its first great divisions. In the ovum of the Rabbit (Barry) and in that of the Dog (Bischoff) they are suspended in the fluid, quite free of the yelk, during the first divisions; they are also on one side of the yelk, usually in the cleft between the primary divisions of the mass; and they continue to be seen at the same place, as in the Amphibia, until about the fourth or fifth subdivision, when they are suddenly lost.

At $4^h\ 15^m$, when the second crucial division of the yelk was nearly completed, I found that the granulated or anterior spherical body floated in the fluid in the first formed furrow, and was as yet unchanged in appearance, saving only that its contents seemed to be divided into two masses; whilst the nucleated or posterior body had already undergone some change, since there appeared in its place a group of four distinct cells: these cells I am disposed to believe, in the absence of proof not yet obtained, were the progeny of the nucleated body that had disappeared.

After this stage the tracing of the vesicles was more difficult. The granulated or anterior body, still unchanged, is seen at the same place when the yelk undergoes its

equatorial or third great subdivision: this cleavage begins on the side of the yelk opposite to that at which the granular body is seen.

After the completion of this equatorial division, the granular-like nucleated body is suddenly lost, and I have been unable to trace it further. But I am not inclined to believe that these bodies are simply dissolved in the fluid surrounding the yelk in the Invertebrata, according to the supposition of Van Beneden, Rathke, Quatrefages and others; supported as this view has been by Professor Bischoff*, who is inclined to think that such may be their ending in the Vertebrata. On the contrary, the regularity of their appearance at a given period, their presence at a particular part of the yelk, their special course on the surface, and their disappearance at a given stage of the yelk-changes, furnish a presumption of their greater importance.

Van Beneden† has already pointed out, notwithstanding his above-mentioned opinion, that it is on that side of the yelk of the *Limax* at which these bodies appear, that the body of the animal is afterwards formed. Also Dumortier‡ had previously believed that the spherical bodies gave origin to the head and foot of the future animal. Although I am unable to specify the exact part which these bodies take in the formation of the embryo, all my observations on the eggs of the Frog and Toad have proved to me that they are usually, and perhaps invariably, at that part of the yelk at which the head of the embryo is afterwards formed. Their isolation from the yelk for a time, during which it is in a very disturbed state, and their constant localization, with their subsequent disappearance in that part at which the head is afterwards to be developed, seem favourable to the conclusion that their function is as definite as their presence is certain.

It has been supposed by F. Müller§ that the spherical bodies determined in the Mollusca the line of the first cleavage of the yelk; and with this idea he named them the *direction* vesicles. But my observations on the development of the embryo lead me to believe, that, though the transit of these bodies is usually in the same line as the first cleft, the direction of the fissure is not determined by them, but is owing to some other cause.

With the view of tracing the origin of these bodies, the egg of the Frog and Toad was examined from a period before the disappearance of the germinal vesicle to the time at which they appear on the yelk after fecundation; and for this purpose the eggs were hardened in rectified spirit and then dissected‖. * * * * *

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* Entwickelungsgeschichte des Meerschweinchens, 1852, p. 19.

† Ann. des Sci. Nat., tom. xv. p. 126, and plate 1, 1841; and Müller's Archiv for 1841, p. 181.

‡ Mém. de l'Acad. de Bruxelles, tom. x. p. 136. § Wiegmann's Archiv for 1848, p. 1.

‖ [The results obtainable from this inquiry are not apparently contained in the MS. note books. It is however well known to the writer that Mr. Newport intended, had his life been spared, to employ those means in learning the *destination* of the spherical bodies; and the circumstance is here mentioned because the mode of investigation seems most judicious, and likely to be useful to any one engaged in prosecuting the inquiry.—G.V.E.]

On the production of the Body and Head of the Embryo from definite portions of the Yelk.

Repeated observations have demonstrated that in one part of the yelk the head, and in another the body and tail of the forthcoming being begin. This appointment of the parts is further indicated, very early, by conditions in the yelk cleavage—conditions so constant that I am able to predicate soon after the completion of the horizontal cleft, or at the beginning of the fourth change, where the head, and where the tail of the future embryo will be placed. In support of this statement the changes in the egg undergoing segmentation must be referred to, but they will be traced, here, only to the point indicatory of the diagnosis to be made.

To ascertain the correctness of the following statement it will be necessary to put the impregnated eggs, dark surface uppermost, in *tube*-cells, and to mark on these where the future head and body should be, according to the deduction from changes in the segmenting yelk.

First change.—In eggs kept at a temperature of 60° Fahr., the first change begins at about the end of four hours, and consists in a cleft that runs vertically round the egg. This cleft may be called *axial* from its position, as it will afterwards appear, to the body of the future embryo. It begins in the centre of the dark surface in a slight depression, so that in some instances the canal may be almost detected: then suddenly a sulcus appears on each side of the depression, and quickly extends outwards around the yelk, though it is deepest and most strongly marked above. In the egg of the Frog as in that of the Newt, the halves are not always of equal size in this stage, but this disproportion is obviated in the second division.

Second change.—Another cleft now surrounds the egg crossing the first at right angles, and this may be named *crucial*. An interval of about an hour elapses before its appearance, and its commencement is not seen at the same instant on each side of the axial line, but is perceived first at one side. After this, as after the axial cleft, the pieces into which it divides the yelk are unequal in size; but these variations have in general but little influence on the result obtained by the segmentation.

In some ova there is such an unusual displacement of the segments as almost to prevent the identification of the parts in the subsequent changes, the lines of the axial and crucial clefts being rendered very irregular by unequal increase of the sectional pieces on opposite sides of the first cleft. This irregularity I am inclined to think arises from unequal division of the yelk in the production of the first cleft; and to it I attribute the partial horizontal movement of the yelk itself, which may be sometimes recognized.

But when the yelk has divided with perfect equality both axially and crucially, the pieces on one side of the crucial line (in front say) always become larger than those on the other side (behind); and during this increase in size the anterior divisions project backwards over the posterior so as to cause a bending of the crucial sulcus, the convexity being forwards.

Third change.—In this a third cleft is formed horizontally around the egg, nearly midway between the upper and under surfaces: this may be called from its position, the *equatorial* cleft.

Fourth change.—About two hours after the completion of the crucial cleft, a new series of changes is set up in the egg. The clefts no longer include the whole circumference of the egg, but are confined to the splitting of the larger into smaller pieces after a binary plan: and this process does not begin at once over the whole surface, but appears first in a given spot, and then pursues a definite course; thus each of the two pieces seen from above on one side (behind) of the crucial cleft become subdivided, producing four segments on one side of that line, whilst there are only two on the other. When this subdivision is nearly completed, and not till then, a corresponding change takes place in the two segments on the other side (in front) of the sulcus.

When this stage of the segmentation of the yelk is arrived at, the position of the body and head of the coming being can be determined with certainty, so that it is not necessary to follow further the changes during segmentation. If the cell be marked opposite the first commencing post-crucial subdivisions, and then set aside for the formation of the embryo, the trunk and tail of the developing being will be found to originate in this first-subdividing part behind the crucial sulcus, and the head to be produced in the part on the other side, or in front of the sulcus, in which the secondary segmentation last appears.

On the correspondence of the primary cleft of the Yelk with the axis of the future Embryo.

I have been long aware that the axis of the embryo was in the line of the first cleft of the yelk, but my endeavour to show this was not always satisfactory, in consequence of the difficulty of making the egg keep a given position, whilst it was free to move; but since I have employed the tube-cell I have obtained the desired evidence with great ease. The results of the following observations will support my statement.

Obs. 1.—I took an egg that had just divided for the first time, and placed it in a glass cell only sufficiently large to contain it when the jelly was fully expanded, and filled the cell with water. The dorsal surface turned uppermost, as usual, consequently I had under my eye the whole surface, and could watch the changes with the microscope. I marked the plate of glass supporting the cell with a line parallel to the primary cleft of the yelk, and indicated the position of the ends of the sulcus by other marks. The whole was placed in a temperature of 60° Fahr.

At the time of the closing-in of the dorsal laminæ, I found the correspondence between the axis of the embryo and the line of the first cleft to be exact. As I knew however that some movement would be excited, I made a drawing of the appearances. In twelve more hours the dorsal sulcus was nearly closed, and the embryo had passed to the left of the line marked on the glass, viz. to about an angle of 30°. A second drawing was made to remove doubts.

On the day after, the embryo had moved still further round. Finally, the embryo was perfected, like those of the same set that were left in mass in water.

Obs. 2.—Nine eggs were put into separate cells on March 11th, and when segmentation began, the line of the first cleft was carefully marked on the glass in the manner before explained. One of the eggs was abortive.

March 13. The dorsal sulcus was forming in three of the embryos exactly in the line of the cleft.

March 14. In each of the eight instances the axis of the body is more or less precisely in the line of the sulcus: thus in five it was in the exact line, in one about five degrees to the left, in another about three degrees to the left, and in the remaining one rather more to the left of the given line.

Obs. 3.—Five eggs were placed in separate cells, and marked, as above directed, and then removed to a high temperature.

March 26. The results obtained from these were confirmatory of the facts before stated, as the variation between the line and the axis of the beings was only slight; the axis of two being directed to the right, one to the left, and one perfectly coinciding.

Although these observations have shown that the axis of the body of the future embryo corresponds primarily with the first cleft in the yelk, they point out that, at times, the axis deviates to the left or right of that line. The cause of this deviation I may attribute to a change in the position of the yelk, for on March 29, 1853, I observed that the entire yelk occasionally shifts its position during the progress of segmentation, in consequence probably of unsymmetrical division, in accordance with the explanation before given at page 240.

On the power of the Spermatozoon to influence in artificial impregnation the direction of the first cleft of the Yelk.

In connexion with the influence of the spermatozoon on the egg, I determined to try whether the artificial application of that body to different parts of the egg's surface could affect the position of the first cleft of the yelk.

Obs. 1.—Several eggs were placed, March 29, in separate tube-cells, with each turned on its side so that both the dark and the white surface were exposed. Very recent spermatic fluid was then applied, by means of a pin's head, to the lower part of the dark surface, and the cell was carefully marked close to the spot, to show where the egg was touched.

The eggs rotated in the usual way, so as to bring upwards the dark surface, and at the end of one hour and a half only two eggs were fecundated. In these the spherical vesicles had the usual position and appearance, and were directed outwards across the centre of the flat surface of the yelk to that side of the egg to which the spermatic fluid had been applied. After the formation of the primary cleft, the cells were marked and set aside for the production of the embryo.

April 3. Each egg has formed an embryo, and in each instance with the head to the side of the egg touched.

Obs. 2.—Four eggs were placed in separate cells as before, and only two became fruitful.

In one the primary cleft was in the precise line of the spot touched, although the egg subsequently diverged to the left; and the head corresponded to the part fecundated. In the other egg the cleft was about ten degrees to the left of the part impregnated, and the head was also turned to the part touched with the fluid.

Obs. 3.—Four other eggs were taken, but two of them were sterile; and in the development of one the head deviated remarkably from the usual position.

The first cleft in one (*a*) was about six degrees to the right; and in the other (*b*) about five degrees to the left of the point touched. Both formed embryos: in one (*a*) the head was at the end of the cleft nearest the point touched, but in the other (*b*) at the end furthest from the same point. The peculiarity in this last experiment I cannot explain; possibly there might be some want of precision in conducting it.

Similar experiments were repeated four other times, and the results showed that the first cleft of the yelk is in a line with the point of the egg artificially impregnated, and that the head of the young frog is turned towards the same point. But in this set, as in the other, the nascent being in the course of its development deviated to the right or the left of a line through the centre of the spot fecundated.

In another set of experiments the spermatic fluid was applied to an unknown part of the egg.

On taking my last female frog (April 5, 1853) I found the white part so dark in colour (not a very unusual change), that the usual black surface could not be well distinguished. Accordingly the eggs were put into separate cells, and the fluid was applied and the cell marked in the usual way, without a knowledge of what was the spot touched.

Experiment 1.—Six eggs were used: all were fecundated, and segmented in about three hours and a half in an atmosphere varying from 61° to 64° Fahr. The following is the result:—

The axis of the embryo was in one in a line with the part touched, in four diverging slightly to the left, and in one to the right of that line. The head was in four nearest to the spot fecundated, and in two furthest from it.

Experiment 2 with five eggs: all of these were fruitful. The axis coincided exactly with the impregnated point in three, and diverged slightly to the left in two eggs. The head was nearest the same point in four, and furthest from it in one embryo.

Experiment 3.—Five eggs were employed, and being fertilized, gave the following result:—

The axis coincided with the given point in one, and diverged more to the right or left in the other instances. The head was nearest the side to which the spermatic fluid was applied in four, and furthest from it in one.

From these and other experiments it results, that, when part of the black surface of the egg was certainly touched with the spermatic fluid, the head of the future embryo was turned towards it in ten eggs, and removed from it in only one; and that the axis of the embryo nearly coincided at first with the line of the point touched, though it afterwards deviated to the left or right of that line (most to the left), the distance not exceeding fifteen degrees.

When however the part of the egg to which the spermatic fluid was applied was not known, the axis kept much the same position as before, but the head was far distant from the impregnated spot in four out of sixteen instances.

IX. *An Introductory Memoir upon Quantics.* By Arthur Cayley, *Esq.*

Received April 20,—Read May 4, 1854.

1. The term Quantics is used to denote the entire subject of rational and integral functions, and of the equations and loci to which these give rise; the word 'quantic' is an adjective, meaning *of such a degree*, but may be used substantively, the noun understood being (unless the contrary appear by the context) function; so used the word admits of the plural 'quantics.'

The quantities or symbols to which the expression 'degree' refers, or (what is the same thing) in regard to which a function is considered as a quantic, will be spoken of as 'facients.' A quantic may always be considered as being, in regard to its facients, homogeneous, since to render it so, it is only necessary to introduce as a facient unity, or some symbol which is to be ultimately replaced by unity; and in the cases in which the facients are considered as forming two or more distinct sets, the quantic may, in like manner, be considered as homogeneous in regard to each set separately.

2. The expression 'an equation,' used without explanation, is to be understood as meaning the equation obtained by putting any quantic equal to zero. I make no absolute distinction between the words 'degree' and 'order' as applied to an equation or system of equations, but I shall in general speak of the order rather than the degree. The equations of a system may be independent, or there may exist relations of connexion between the different equations of the system; the subject of a system of equations so connected together is one of extreme complexity and difficulty. It will be sufficient to notice here, that in any system whatever of equations, assuming only that the equations are not more than sufficient to determine the ratios of the facients, and joining to the system so many linear equations between the facients as will render the ratios of the facients determinate, the order of the system is the same thing as the order of the equation which determines any one of these ratios; it is clear that for a single equation the order so determined is nothing else than the order of the equation.

3. An equation or system of equations represents, or is represented by a locus. This assumes that the facients depend upon quantities x, y, ... the coordinates of a point in space; the entire series of points the coordinates of which satisfy the equation or system of equations, constitutes the locus. To avoid complexity, it is proper to take the facients themselves as coordinates, or at all events to consider these facients as linear functions of the coordinates; this being the case, the order of the locus will be the order of the equation or system of equations.

4. I have spoken of the *coordinates* of a *point* in *space*. I consider that there is an ideal space of any number of dimensions, but of course, in the ordinary acceptation of the word, space is of three dimensions; however, the plane (the space of ordinary plane geometry) is a space of two dimensions, and we may consider the line as a space of one dimension. I do not, it should be observed, say that the only idea which can be formed of a space of two dimensions is the plane, or the only idea which can be formed of space of one dimension is the line; this is not the case. To avoid complexity, I will take the case of plane geometry rather than geometry of three dimensions; it will be unnecessary to speak of space, or of the number of its dimensions or of the plane, since we are only concerned with space of two dimensions, viz. the plane; I say, therefore, simply that x, y, z are the coordinates of a point (strictly speaking, it is the ratios of these quantities which are the coordinates, and the quantities x, y, z themselves are indeterminate, *i. e.* they are only determinate to a common factor *près*, so that in assuming that the coordinates of a point are α, β, γ, we mean only that $x:y:z=\alpha:\beta:\gamma$, and we never as a result obtain $x, y, z=\alpha, \beta, \gamma$, but only $x:y:z=\alpha:\beta:\gamma$; but this being once understood, there is no objection to speaking of x, y, z as coordinates). Now the notions of coordinates and of a point are merely relative; we may, if we please, consider $x:y:z$ as the parameters of a curve containing two variable parameters; such curve becomes of course determinate when we assume $x:y:z=\alpha:\beta:\gamma$, and this very curve is nothing else than the point whose coordinates are α, β, γ, or as we may for shortness call it, the point (α, β, γ). And if the coordinates (x, y, z) are connected by an equation, then giving to these coordinates the entire system of values which satisfy the equation, the locus of the points corresponding to these values is the locus representing or represented by the equation; this of course fixes the notion of a curve of any order, and in particular the notion of a line as the curve of the first order.

The theory includes as a very particular case, the ordinary theory of reciprocity in plane geometry; we have only to say that the word 'point' shall mean 'line,' and the word 'line' shall mean 'point,' and that expressions properly or primarily applicable to a point and a line respectively shall be construed to apply to a line and a point respectively, and any theorem (assumed of course to be a purely descriptive one) relating to points and lines will become a corresponding theorem relating to lines and points; and similarly with regard to curves of a higher order when the ideas of reciprocity applicable to these curves are properly developed.

5. A quantic of the degrees $m, m'..$ in the sets $(x, y..), (x', y'..)$ &c. will for the most part be represented by a notation such as

$$(*)(x, y..)^{m}(x', y'..)^{m'}..),$$

where the mark $*$ may be considered as indicative of the absolute generality of the quantic; any such quantic may of course be considered as the sum of a series of terms $x^{\alpha}y^{\beta}..x'^{\alpha'}y'^{\beta'}..$, &c. of the proper degrees in the different sets respectively, each

term multiplied by a coefficient; these coefficients may be mere numerical multiples of single letters or elements such as $a, b, c..$, or else functions (in general rational and integral functions) of such elements; this explains the meaning of the expression 'the elements of a quantic'; in the case where the coefficients are mere numerical multiples of the elements, we may in general speak indifferently of the elements, or of the coefficients. I have said that the coefficients may be numerical multiples of single letters or elements such as $a, b, c..$ By the appropriate numerical coefficient of a term $x^{\alpha}y^{\beta}..x'^{\alpha'}y'^{\beta'}..$, I mean the coefficient of this term in the expansion of

$$(x+y...)^{m}\ (x'+y'..)^{m'}..);$$

and I represent by the notation

$$(a, b..)(x, y..)^{m}(x', y'..)^{m'}..),$$

a quantic in which each term is multiplied as well by its appropriate numerical coefficient as by the literal coefficient or element which belongs to it in the set $(a, b...)$ of literal coefficients or elements. On the other hand, I represent by the notation

$$(a, b..)[x, y..)^{m}(x', y'..)^{m'}..),$$

a quantic in which each term is multiplied only by the literal coefficient or element which belongs to it in the set $(a, b...)$ of literal coefficients or elements. And a like distinction applies to the case where the coefficients are functions of the elements $(a, b, ...)$.

6. I consider now the quantic

$$(*)(x, y..)^{m}(x', y'..)^{m'}..),$$

and selecting any two facients of the same set, *e. g.* the facients x, y, I remark that there is always an operation upon the elements, tantamount as regards the quantic to the operation $x\partial_y$; viz. if we differentiate with respect to each element, multiply by proper functions of the elements and add, we obtain the same result as by differentiating with ∂_y and multiplying by x. The simplest example will show this as well as a formal proof: for instance, as regards $3ax^3+bxy+5cy^3$ (the numerical coefficients are taken haphazard), we have $\frac{1}{3}b\partial_a+10c\partial_b$ tantamount to $x\partial_y$; as regards $a(x-\alpha y)(x-\beta y)$, we have $-a(\alpha+\beta)\partial_a+\alpha^2\partial_a+\beta^2\partial_\beta$ tantamount to $x\partial_y$, and so in any other case. I represent by $\{x\partial_y\}$ the operation upon the elements tantamount to $x\partial_y$, and I write down the series of operations

$$\{x\partial_y\}-x\partial_y, ..\quad \{x'\partial_{y'}\}-x'\partial_{y'}, ..$$

where x, y are considered as being successively replaced by every permutation of two different facients of the set $(x, y..)$; x', y' as successively replaced by every permutation of two different facients of the set $(x', y'..)$, and so on; this I call an entire system, and I say that it is made up of partial systems corresponding to the different facient sets respectively; it is clear from the definition that the quantic is reduced to

zero by each of the operations of the entire system. Now, besides the quantic itself, there are a variety of other functions which are reduced to zero by each of the operations of the entire system; any such function is said to be a covariant of the quantic, and in the particular case in which it contains only the elements, an invariant. (It would be allowable to define as a covariant *quoad any set or sets*, a function which is reduced to zero by each of the operations of the corresponding partial system or systems, but this is a point upon which it is not at present necessary to dwell.)

7. The definition of a covariant may however be generalized in two directions: we may instead of a single quantic consider two or more quantics; the operations $\{x\partial_y\}$, although represented by means of the same symbols x, y, have, as regards the different quantics, different meanings, and we may form the sum $\Sigma\{x\partial_y\}$, where the summation refers to the different quantics: we have only to consider in place of the system before spoken of, the system

$$\Sigma\{x\partial_y\} - x\partial_y, \ldots \quad \Sigma\{x'\partial_{y'}\} - x'\partial_{y'}, \ldots \text{ \&c. \&c.},$$

and we obtain the definition of a covariant of two or more quantics.

Again, we may consider in connexion with each set of facients any number of new sets, the facients in any one of these new sets corresponding each to each with those of the original set; and we may admit these new sets into the covariant. This gives rise to a sum $S(x\partial_y)$, where the summation refers to the entire series of corresponding sets. We have in place of the system spoken of in the original definition, to consider the system

$$\{x\partial_y\} - S(x\partial_y), \ldots \{x'\partial_{y'}\} - S(x'\partial_{y'}), \ldots \text{ \&c. \&c.},$$

or if we are dealing with two or more quantics, then the system

$$\Sigma\{x\partial_y\} - S(x\partial_y), \ldots \Sigma\{x'\partial_{y'}\} - S(x'\partial_{y'}), \ldots \text{ \&c. \&c.},$$

and we obtain the generalized definition of a covariant.

8. A covariant has been defined simply as a function reduced to zero by each of the operations of the entire system. But in dealing with given quantics, we may without loss of generality consider the covariant as a function of the like form with the quantic, *i. e.* as being a rational and integral function homogeneous in regard to the different sets separately, and as being also a rational and integral function of the elements. In particular in the case where the coefficients are mere numerical multiples of the elements, the covariant is to be considered as a rational and integral function homogeneous in regard to the different sets separately, and also homogeneous in regard to the coefficients or elements. And the term 'covariant' includes, as already remarked, 'invariant.'

It is proper to remark, that if the same quantic be represented by means of different sets of elements, then the symbols $\{x\partial_y\}$ which correspond to these different forms of the same quantic are mere transformations of each other, *i. e.* they become in virtue of the relations between the different sets of elements identical.

9. What precedes is a return to and generalization of the method employed in the first part of the memoir published in the Cambridge and Dublin Mathematical Journal, Old Series, t. iv., and New Series, t. i., under the title "On Linear Transformations," and CRELLE, t. xxx., under the title "Mémoire sur les Hyperdéterminants," and which I shall refer to as my original memoir. I there consider in fact the invariants of a quantic

$$(*\,|\,x_1, x_2..x_m\,|\,y_1, y_2..y_m)..)$$

linear in regard to n sets each of them of m facients, and I represent the coefficients of a term $x_\alpha y_\beta z_\gamma..$ by $rst..$ There is no difficulty in seeing that α, β, being any two different numbers out of the series $1, 2..m$, the operation $\{x_\beta \partial_{x_\alpha}\}$ is identical with the operation

$$\Sigma\Sigma..\left(\alpha st..\frac{d}{d\beta st..}\right),$$

where the summations refer to $s, t..$ which pass respectively from 1 to m, both inclusive; and the condition that a function, assumed to be an invariant, *i. e.* to contain only the coefficients, may be reduced to zero by the operation $\{x_\beta \partial_{x_\alpha}\} - x_\beta \partial_{x_\alpha}$, is of course simply the condition that such function may be reduced to zero by the operation $\{x_\beta \partial_{x_\alpha}\}$; the condition in question is therefore the same thing as the equation

$$\Sigma\Sigma..\left(\alpha st..\frac{d}{d\beta st..}\right)u = 0$$

of my original memoir.

10. But the definition in the present memoir includes also the method made use of in the second part of my original memoir. This method is substantially as follows: consider for simplicity a quantic $U =$

$$(*\,|\,x, y..)^n$$

containing only the single set $(x, y..)$, and let $U_1, U_2..$ be what the quantic becomes when the set $(x, y..)$ is successively replaced by the sets $(x_1, y_1..)$, $(x_2, y_2..)$, ... the number of these new sets being equal to or greater than the number of facients in the set. Suppose that A, B, C.. are any of the determinants

$$\begin{Vmatrix} \partial_x, & \partial_{x_1}, & \partial_{x_2}, \ldots \\ \partial_y, & \partial_{y_1}, & \partial_{y_2}, \\ \cdot & & \\ \cdot & & \end{Vmatrix}$$

then forming the derivative

$$A^p B^q C^r .. U_1 U_2 \ldots,$$

where $p, q, r..$ are any positive integers, the function so obtained is a covariant involving the sets $(x_1, y_1..)$, $(x_2, y_2..)$ &c.; and if after the differentiations we replace these sets by the original set $(x, y..)$, we have a covariant involving only the original

set $(x, y..)$ and of course the coefficients of the quantic. It is in fact easy to show that any such derivative is a covariant according to the definition given in this Memoir. But to do this some preliminary explanations are necessary.

11. I consider any two operations P, Q, involving each or either of them differentiations in respect of variables contained in the other of them. It is required to investigate the effect of the operation P.Q, where the operation Q is to be in the first place performed upon some operand Ω, and the operation P is then to be performed on the operand $Q\Omega$. Suppose that P involves the differentiations $\partial_a, \partial_b..$ in respect of variables $a, b..$ contained in Q and Ω, we must as usual in the operation P replace $\partial_a, \partial_b, ..$ by $\partial_a+\partial'_a, \partial_b+\partial'_b, ..$ where the unaccentuated symbols operate only upon Ω, and the accentuated symbols operate only upon Q. Suppose that P is expanded in ascending powers of the symbols $\partial'_a, \partial'_b..$, viz. in the form $P+P_1+P_2+$ &c., we have first to find the values of P_1Q, P_2Q, &c., by actually performing upon Q as operand the differentiations $\partial'_a, \partial'_b..$ The symbols PQ, P_1Q, P_2Q, &c. will then contain only the differentiations $\partial_a, \partial_b..$ which operate upon Ω, and the meaning of the expression being once understood, we may write

$$P.Q=PQ+P_1Q+P_2Q+ \&c.$$

In particular if P be a linear function of $\partial_a, \partial_b..$, we have to replace P by $P+P_1$, where P_1 is the same function of $\partial'_a, \partial'_b..$ that P is of $\partial_a, \partial_b..$, and it is therefore clear that we have in this case

$$P.Q=PQ+P(Q),$$

where on the right-hand side in the term PQ the differentiations $\partial_a, \partial_b, ..$ are considered as not in anywise affecting the symbol Q, while in the term P(Q) these differentiations, or what is the same thing, the operation P, is considered to be performed upon Q as operand.

Again, if Q be a linear function of $a, b, c..$, then $P_2Q=0$, $P_3Q=0$, &c., and therefore $P.Q=PQ+P_1Q$; and I shall in this case also (and consequently whenever $P_2Q=0$, $P_3Q=0$, &c.) write

$$P.Q=PQ+P(Q),$$

where on the right-hand side in the term PQ the differentiations $\partial_a, \partial_b..$ are considered as not in anywise affecting the symbol Q, while the term P(Q) is in each case what has been in the first instance represented by P_1Q.

We have in like manner, if Q be a linear function of $\partial_a, \partial_b, \partial_c...$, or if P be a linear function of $a, b, c...$,

$$Q.P=QP+Q(P);$$

and from the two equations (since obviously $PQ=QP$) we derive

$$P.Q-Q.P=P(Q)-Q(P),$$

which is the form in which the equations are most frequently useful.

12. I return to the expression

$$A^{\alpha}B^{\beta}C^{\gamma}..U_1U_2..,$$

and I suppose that after the differentiations the sets $(x_1, y_1..)$, $(x_2, y_2..)$, &c. are replaced by the original set $(x, y..)$. To show that the result is a covariant, we must prove that it is reduced to zero by an operation $\mathfrak{D}=$

$$\{x\partial_y\}-x\partial_y.$$

It is easy to see that the change of the sets $(x_1, y_1..)$, $(x_2, y_2..)$, &c. into the original set $(x, y..)$ may be deferred until after the operation $\mathfrak{D}$, provided that $x\partial_y$ is replaced by $x_1\partial_{y_1}+x_2\partial_{y_2}+..$, or if we please by $Sx\partial_y$; we must therefore write $\mathfrak{D}=\{x\partial_y\}-Sx\partial_y$. Now in the equation

$$A.\mathfrak{D}-\mathfrak{D}.A=A(\mathfrak{D})-\mathfrak{D}(A),$$

where, as before, $A(\mathfrak{D})$ denotes the result of the operation A performed upon $\mathfrak{D}$ as operand, and similarly $\mathfrak{D}(A)$ the result of the operation $\mathfrak{D}$ performed upon A as operand, we see first that $A(\mathfrak{D})$ is a determinant two of the lines of which are identical, it is therefore equal to zero; and next, since $\mathfrak{D}$ does not involve any differentiations affecting A, that $\mathfrak{D}(A)$ is also equal to zero. Hence $A.\mathfrak{D}-\mathfrak{D}.A=0$ or A and $\mathfrak{D}$ are convertible. But in like manner $\mathfrak{D}$ is convertible with B, C, &c., and consequently $\mathfrak{D}$ is convertible with $A^{\alpha}B^{\beta}C^{\gamma}..$ Now $\mathfrak{D}U_1U_2..=0$. Hence

$$\mathfrak{D}.A^{\alpha}B^{\beta}C^{\gamma}..U_1U_2..=0,$$

or $A^{\alpha}B^{\beta}C^{\gamma}..U_1U_2..$ is a covariant, the proposition which was to be proved.

13. I pass to a theorem which leads to another method of finding the covariants of a quantic. For this purpose I consider the quantic

$$(*)(x, y..)^m(x', y'..)^{m'}..),$$

the coefficients of which are mere numerical multiples of the elements $(a, b, c..)$; and in connexion with this quantic I consider the linear functions $\xi x+\eta y..$, $\xi' x'+\eta' y'..$, which treating $(\xi, \eta..)$, $(\xi', \eta'..)$, &c. as coefficients, may be represented in the form

$$(\xi, \eta..)(x, y..), \quad (\xi', \eta'..)(x', y'..), ..$$

we may from the quantic (which for convenience I call U) form an operative quantic

$$(*)(\xi, \eta..)^m(\xi', \eta'..)^{m'}..)$$

(I call this quantic Θ), the coefficients of which are mere numerical multiples of $\partial_a, \partial_b, \partial_c..$, and which is such that

$$\Theta U=(\xi, \eta..)(x, y..)^m(\xi', \eta'..)(x', y'..)^{m'}..$$

i. e. a product of powers of the linear functions. And it is to be remarked that as regards the quantic Θ and its covariants or other derivatives, the symbols $\partial_a, \partial_b, \partial_c..$ are to be considered as elements with respect to which we may differentiate, &c. The quantic Θ gives rise to the symbols $\{\xi\partial_x\}$, &c. analogous to the symbols $\{x\partial_y\}$, &c. formed from the quantic U. Suppose now that Φ is any quantic containing as well

the coefficients as all or any of the sets of Θ. Then $\{x\partial_y\}$ being a linear function of $a, b, c..$ the variables to which the differentiations in Φ relate, we have

$$\Phi.\{x\partial_y\}=\Phi\{x\partial_y\}+\Phi(\{x\partial_y\}).$$

Again, $\{\eta\partial_\xi\}$ being a linear function of the differentiations with respect to the variables $\partial_a, \partial_b, \partial_c..$ in Φ, we have

$$\{\eta\partial_\xi\}.\Phi=\{\eta\partial_\xi\}\Phi+\{\eta\partial_\xi\}(\Phi).$$

And these equations serve to show the meaning of the notations $\Phi(\{x\partial_y\})$ and $\{\eta\partial_\xi\}(\Phi)$, and there exists between these symbols the singular equation

$$\Phi(\{x\partial_y\})=\{\eta\partial_\xi\}(\Phi).$$

14. The general demonstration of this equation presents no real difficulty, but to avoid the necessity of fixing upon a notation to distinguish the coefficients of the different terms and for the sake of simplicity, I shall merely exhibit by an example the principle of such general demonstration. Consider the quantic

$$U=ax^3+3bx^2y+3cy^2+dy^3,$$

this gives

$$\Theta=\xi^3\partial_a+\xi^2\eta\partial_b+\xi\eta^2\partial_c+\eta^3\partial_d;$$

or if, for greater clearness, $\partial_a, \partial_b, \partial_c, \partial_d$ are represented by $\alpha, \beta, \gamma, \delta$, then

$$\Theta=\alpha\xi^3+\beta\xi^2\eta+\gamma\xi\eta^2+\delta\eta^3,$$

and we have

$$\{x\partial_y\}=3b\partial_a+2c\partial_b+d\partial_c$$

and

$$\{\eta\partial_\xi\}=3a\partial_\beta+2\beta\partial_\gamma+\gamma\partial_\delta.$$

Now considering Φ as a function of $\partial_a, \partial_b, \partial_c, \partial_d$, or what is the same thing, of $\alpha, \beta, \gamma, \delta$, we may write

$$\Phi(\{x\partial_y\})=\Phi(3b\alpha+2c\beta+d\gamma);$$

and if in the expression of Φ we write $\alpha+\partial_a, \beta+\partial_b, \gamma+\partial_c, \delta+\partial_d$ for $\alpha, \beta, \gamma, \delta$ (where only the symbols $\partial_a, \partial_b, \partial_c, \partial_d$ are to be considered as affecting a, b, c, d as contained in the operand $3b\alpha+2c\beta+d\gamma$), and reject the first term or term independent of $\partial_a, \partial_b, \partial_c, \partial_d$ in the expansion, we have the required value of $\Phi(\{x\partial_y\})$. This value is

$$(\partial_a\Phi\partial_\alpha+\partial_\beta\Phi\partial_b+\partial_\gamma\Phi\partial_c)(3b\alpha+2c\beta+d\gamma);$$

or performing the differentiations $\partial_a, \partial_b, \partial_c, \partial_d$, the value is

$$(3a\partial_\beta+2\beta\partial_\gamma+\gamma\partial_\delta)\Phi,$$

i. e. we have

$$\Phi(\{x\partial_y\})=\{\eta\partial_\xi\}(\Phi).$$

15. Suppose now that Φ is a covariant of Θ, then the operation Φ performed upon any covariant of U gives rise to a covariant of the system

$$(*\,|\,x, y..|\,x', y'..|\,x''..),$$
$$(\xi, \eta..|\,x, y..), \qquad (\xi', \eta'..|\,x', y'..), \text{ \&c.}$$

To prove this it is to be in the first instance noticed, that as regards $(\xi, \eta..|\,x, y..)$, &c. we have $\{x\partial_y\}=\eta\partial_\xi$, &c. Hence considering $\{x\partial_y\}$, &c. as referring to the quantic U,

the operation $\Sigma\{x\partial_y\}-x\partial_y$ will be equivalent to $\{x\partial_y\}+\eta\partial_\xi-x\partial_y$, and therefore every covariant of the system must be reduced to zero by each of the operations

$$\mathfrak{D}=\{x\partial_y\}+\eta\partial_\xi-x\partial_y.$$

This being the case, we have

$$\mathfrak{D}.\Phi=\mathfrak{D}\Phi+\mathfrak{D}(\Phi)$$

$$\Phi.\mathfrak{D}=\Phi\mathfrak{D}+\Phi(\mathfrak{D}),$$

equations which it is obvious may be replaced by

$$\mathfrak{D}.\Phi=\mathfrak{D}\Phi+\eta\partial_\xi(\Phi)$$

$$\Phi.\mathfrak{D}=\Phi\mathfrak{D}+\Phi(\{x\partial_y\}),$$

and consequently (in virtue of the theorem) by

$$\mathfrak{D}.\Phi=\mathfrak{D}\Phi+\eta\partial_\xi(\Phi)$$

$$\Phi.\mathfrak{D}=\Phi\mathfrak{D}+\{\eta\partial_\xi\}(\Phi);$$

and we have therefore $\mathfrak{D}.\Phi-\Phi.\mathfrak{D}=-(\{\eta\partial_\xi\}-\eta\partial_\xi)(\Phi)$;

or, since Φ is a covariant of Θ, we have $\mathfrak{D}.\Phi=\Phi.\mathfrak{D}$. And since every covariant of the system is reduced to zero by the operation $\mathfrak{D}$, and therefore by the operation $\Phi.\mathfrak{D}$, such covariant will also be reduced to zero by the operation $\mathfrak{D}.\Phi$, or what is the same thing, the covariant operated on by Φ, is reduced to zero by the operation $\mathfrak{D}$ and is therefore a covariant, *i. e.* Φ operating upon a covariant gives a covariant.

16. In the case of a quantic such as U=

$$(*\,\overset{m}{\backslash}x, y\overset{m'}{\backslash}x', y')..),$$

we may instead of the new sets (ξ, η), (ξ', η').. employ the sets $(y, -x)$, $(y', -x')$, &c. The operative quantic Θ is in this case defined by the equation $\Theta U=0$, and if Φ be, as before, any covariant of Θ, then Φ operating upon a covariant of U will give a covariant of U. The proof is nearly the same as in the preceding case; we have instead of the equation $\Phi(\{x\partial_y\})=\{\eta\partial_\xi\}(\Phi)$ the analogous equation

$$\Phi(\{x\partial_y\})=-\{x\partial_y\}(\Phi),$$

where on the left-hand side $\{x\partial_y\}$ refers to U, but on the right-hand side $\{x\partial_y\}$ refers to Θ, and instead of $\mathfrak{D}=\{x\partial_y\}+\eta\partial_\xi-x\partial_y$ we have simply $\mathfrak{D}=\{x\partial_y\}-x\partial_y$.

17. I pass next to the quantic

$$(*\,\backslash x, y)^m,$$

which I shall in general consider under the form

$$(a, b..b', a'\backslash x, y)^m,$$

but sometimes under the form

$$(a, b...b', a'\overset{m}{\backslash}x, y)^m,$$

the former notation denoting, it will be remembered,

$$ax^m+\frac{m}{1}bx^{m-1}y..+\frac{m}{1}b'xy^{m-1}+a'y^m,$$

and the latter notation

$$ax^m+bx^{m-1}y..+b'xy^{m-1}+a'y^m.$$

But in particular cases the coefficients will be represented all of them by unaccentuated letters, thus $(a, b, c, d)(x, y)^3$ will be used to denote $ax^3+3bx^2y+3cxy^2+dy^3$, and $(a, b, c, \partial)(x, y)^3$ will be used to denote $ax^3+bx^2y+cxy^2+dy^3$, and so in all similar cases.

Applying the general methods to the quantic

$$(a, b..b', a')(x, y)^m,$$

we see that

$$\{y\partial_x\}=a\partial_b+2b\partial_c...+mb'\partial_{a'}$$

$$\{x\partial_y\}=mb\partial_a+(m-1)c\partial_b..+a'\partial_{b'};$$

in fact, with these meanings of the symbols the quantic is reduced to zero by each of the operations $\{y\partial_x\}-y\partial_x$, $\{x\partial_y\}-x\partial_y$; hence according to the definition any function which is reduced to zero by each of the last-mentioned operations is a covariant of the quantic. But in accordance with a preceding remark, the covariant may be considered as a rational and integral function, separately homogeneous in regard to the facients (x, y) and the coefficients $(a, b..b', a')$. If instead of the single set (x, y) the covariant contains the sets (x_1, y_1), (x_2, y_2), &c., then it must be reduced to zero by each of the operations $\{y\partial_x\}-Sy\partial_x$, $\{x\partial_y\}-Sx\partial_y$ (where $Sy\partial_x=y_1\partial_{x_1}+y_2\partial_{x_2}+..$), but I shall principally attend to the case in which the covariant contains only the set (x, y).

Suppose, for shortness, that the quantic is represented by U, and let U_1, U_2.. be what U becomes when the set (x, y) is successively replaced by the sets (x_1, y_1), (x_2, y_2), &c. Suppose moreover that $\overline{12}=\partial_{x_1}\partial_{y_2}-\partial_{x_2}\partial_{y_1}$ &c., then the function

$$\overline{12}^p\overline{13}^q\overline{23}^r..U_1U_2U_3..,$$

in which, after the differentiations, the new sets (x_1, y_1), (x_2, y_2).. may be replaced by the original set (x, y)—, will be a covariant of the quantic U. And if the number of differentiations be such as to make the facients disappear, *i. e.* if the sum of all the indices p, q.. of the terms $\overline{12}$, &c. which contain the symbolic number 1, the sum of all the indices p, r, &c. of the terms which contain the symbolic number 2, and so on, be severally equal to the degree of the quantic, we have an invariant. The operative quantic Θ becomes in the case under consideration

$$\Theta=(\partial_{a'}, -\partial_{b'}...\pm\partial_{a}](x, y)^m,$$

the signs being alternately positive and negative; in fact it is easy to verify that this expression gives identically $\Theta U=0$, and any covariant of Θ operating on a covariant of U gives rise to a covariant of U.

18. But the quantic

$$(a, b..b', a')(x, y)^m,$$

considered as decomposable into linear factors, *i. e.* as expressible in the form

$$a(x-\alpha y)(x-\beta y)..,$$

gives rise to a fresh series of results. We have in this case

$$\{y\partial_x\} = \partial_\alpha + \partial_\beta ..$$

$$\{x\partial_y\} = -(\alpha+\beta..)a\partial_\alpha + \alpha^2\partial_\alpha + \beta^2\partial_\beta + .. ;$$

in fact with these meanings of the symbols the quantic is reduced to zero by each of the operations $\{x\partial_y\} - x\partial_y$, $\{y\partial_x\} - y\partial_x$, and we have consequently the definition of the covariant of a quantic considered as expressed in the form $a(x-\alpha y)(x-\beta y)..$ And it will be remembered that these and the former values of the symbols $\{x\partial_y\}$ and $\{y\partial_x\}$ are, when the same quantic is considered as represented under the two forms $(a, b, .b', a'\chi(x, y)^m$ and $a(x-\alpha y)(x-\beta y)..$, identical.

19. Consider now the expression

$$a^\theta(x-\alpha y)^j(x-\beta y)^k..(\alpha-\beta)^p..),$$

where the sum of the indices $j, p...$ of all the simple factors which contain α, the sum of the indices $k, p...$ of all the simple factors which contain β, &c. are respectively equal to the index θ of the coefficient a. The index θ and the indices p, &c. may be considered as arbitrary, nevertheless within such limits as will give positive values (0 inclusive) for the indices $j, k, ...$

The expression in question is reduced to zero by each of the operations $\{x\partial_y\} - x\partial_y$, $\{y\partial_x\} - y\partial_x$; and this is of course also the case with the expressions obtained by interchanging in any manner the roots $\alpha, \beta, \gamma..$, and therefore with the expression

$$a^\theta\Sigma(x-\alpha y)^j(x-\beta y)^k..(\alpha-\beta)^p..),$$

where Σ denotes a summation with respect to all the different permutations of the roots $\alpha, \beta...$

The function so obtained (which is of course a rational function of $a, b..b', a'$) will be a covariant, and if we suppose $\mu = m\theta - 2Sp$, where Sp denotes the sum of all the indices p of the different terms $(\alpha-\beta)^p$, &c., then the covariant will be of the order μ (*i. e.* of the degree μ in the facients x, y), and of the degree θ in the coefficients.

20. In connexion with this covariant

$$a^\theta\Sigma(x-\alpha y)^p(x-\beta y)^k..(\alpha-\beta)^p..)$$

of the order μ and of the degree θ in the coefficients, of the quantic $U =$

$$a(x-\alpha y)(x-\beta y)..,$$

consider the covariant

$$\Sigma(\overline{12}^p..)V_1V_2..V_m$$

of a quantic $V =$

$$(*\chi(x, y)^\phi,$$

in which, after the differentiations, the sets (x_1, y_1), $(x_2, y_2)..$ are replaced by the original set (x, y). The last-mentioned covariant will be of the order $m(\varphi-\theta)+\mu$, and will be of the degree m in the coefficients; and in particular if $\varphi = \theta$, *i. e.* if V be a quantic of the order θ, then the covariant will be of the order μ and of the degree

m in the coefficients. Hence to a covariant of the degree θ in the coefficients, of a quantic of the order m, there corresponds a covariant of the degree m in the coefficients, of a quantic of the order θ; the two covariants in question being each of them of the same order μ. And it is proper to notice, that if we had commenced with the covariant of the quantic V, a reverse process would have led to the covariant of the quantic U. We may, therefore, say that the covariants of a given order and of the degree θ in the coefficients, of a quantic of the order m, correspond each to each with the covariants of the same order and of the degree m in the coefficients, of a quantic of the order θ; and in particular the invariants of the degree θ of a quantic of the order m, correspond each to each with the invariants of the degree m of a quantic of the order θ. This is the law of reciprocity demonstrated by M. HERMITE, by a method which (I am inclined to think) is substantially identical with that here made use of, although presented in a very different form: the discovery of the law, considered as a law relating to the *number* of invariants, is due to Mr. SYLVESTER. The precise meaning of the law, in the last-mentioned point of view, requires some explanation. Suppose that we know all the really independent invariants of a quantic of the order m, the law gives the number of invariants of the degree m of a quantic of the order θ (it is convenient to assume $\theta > m$), viz. of the invariants of the degree in question, which are linearly independent, or asyzygetic, *i. e.* such that there do not exist any merely numerical multiples of these invariants having the sum zero, but the invariants in question may and in general will be connected *inter se* and with the other invariants of the quantic to which they belong by non-linear equations; and in particular the system of invariants of the degree m will comprise all the invariants of that degree (if any) which are rational and integral functions of the invariants of lower degrees. The like observations apply to the system of covariants of a given order and of the degree m in the coefficients, of a quantic of the order θ.

21. The number of the really independent covariants of a quantic $(*\chi x, y)^m$ is precisely equal to the order m of the quantic, *i. e.* any covariant is a function (generally an irrational function only expressible as the root of an equation) of any m independent covariants, and in like manner the number of really independent invariants is $\overline{m-2}$; we may, if we please, take $\overline{m-2}$ really independent invariants as part of the system of the m independent covariants; the quantic itself may be taken as one of the other two covariants, and any other covariant as the other of the two covariants; we may therefore say that every covariant is a function (generally an irrational function only expressible as the root of an equation) of $\overline{m-2}$ invariants, of the quantic itself and of a given covariant.

22. Consider any covariant of the quantic

$$(a, b..b', a'\chi x, y)^m,$$

and let this be of the order μ, and of the degree θ in the coefficients. It is very easily shown that $m\theta - \mu$ is necessarily even. In particular in the case of an invariant

(*i. e.* when $\mu=0$) $m\theta$ is necessarily even*; so that a quantic of an odd order admits only of invariants of an even degree. But there is an important distinction between the cases of $m\theta-\mu$ evenly even and oddly even. In the former case the covariant remains unaltered by the substitution of (y, x), $(a', b', .. b, a)$ for (x, y), $(a, b, .. b', a')$; in the latter case the effect of the substitution is to change the sign of the covariant. The covariant may in the former case be called a symmetric covariant, and in the latter case a skew covariant. It may be noticed in passing, that the simplest skew invariant is M. HERMITE's invariant of the 18th degree of a quantic of the 5th order.

23. There is another very simple condition which is satisfied by every covariant of the quantic

$$(a, b..b', a'\chi(x, y)^m,$$

viz. if we consider the facients (x, y) as being respectively of the weights $\frac{1}{2}$, $-\frac{1}{2}$, and the coefficients $(a, b..b', a')$ as being respectively of the weights $-\frac{1}{2}m$, $-\frac{1}{2}m+1$, $..\frac{1}{2}m-1$, $\frac{1}{2}m$, then the weight of each term of the covariant will be zero. This is the most elegant statement of the law, but to avoid negative quantities, the statement may be modified as follows:—if the facients (x, y) are considered as being of the weights 1, 0 respectively, and the coefficients $(a, b..b', a')$ as being of the weights $0, 1..\overline{m-1}, m$ respectively, then the weight of each term of the covariant will be $\frac{1}{2}(m\theta+\mu)$.

24. The preceding laws as to the form of a covariant have been stated here by way of anticipation, principally for the sake of the remark, that they so far define the form of a covariant as to render it in very many cases practicable with a moderate amount of labour to complete the investigations by means of the operations $\{x\partial_y\}-x\partial_y$ and $\{y\partial_x\}-y\partial_x$. In fact, for finding the covariants of a given order, and of a given degree in the coefficients, we may form the most general function of the proper order and degree in the coefficients, satisfying the prescribed conditions as to symmetry and weight: such function, if reduced to zero by one of the operations in question, will, on account of the symmetry, be reduced to zero by the other of the operations in question; it is therefore only necessary to effect upon it, *e. g.* the operation $\{x\partial_y\}-x\partial_y$, and to determine if possible the indeterminate coefficients in such manner as to render the result identically zero: of course when this cannot be done there is not any covariant of the form in question. It is moreover proper to remark, as regards invariants, that if an invariant be expanded in a series of ascending powers of the first coefficient a, and the first term of the expansion is known, all the remaining terms can be at once deduced by mere differentiations. There is one very important case in which the value of such first term (*i. e.* the value of the invariant when a is put equal to 0) can be deduced from the corresponding invariant of a quantic of the

* I may remark that it was only M. HERMITE's important discovery of an invariant of the degree 18 of a quantic of the order 5, which removed an erroneous impression which I had been under from the commencement of the subject, that $m\theta$ was of necessity *evenly even*.

next inferior order; the case in question is that of the discriminant (or function which equated to zero expresses the equality of a pair of roots); for by JOACHIMSTHAL'S theorem, if in the discriminant of the quantic $(a, b..b', a'\chi(x, y))^m$ we write $a=0$, the result contains b' as a factor, and divested of this factor is precisely the discriminant of the quantic of the order $\overline{m-1}$ obtained from the given quantic by writing $a=0$ and throwing out the factor x: this is in practice a very convenient method for the calculation of the discriminants of quantics of successive orders. It is also to be noticed as regards covariants, that when the first or last coefficient of any covariant (*i. e.* the coefficient of the highest power of either of the facients) is known, all the other coefficients can be deduced by mere differentiations.

POSTSCRIPT added October 7th, 1854.—I have, since the preceding memoir was written, found with respect to the covariants of a quantic $(*\chi(x, y))^m$, that a function of any order and degree in the coefficients satisfying the necessary condition as to weight, and such that it is reduced to zero by one of the operations $\{x\partial_y\}-x\partial_y$, $\{y\partial_x\}-y\partial_y$, will of necessity be reduced to zero by the other of the two operations, *i. e.* it will be a covariant; and I have been thereby led to the discovery of the law for the number of asyzygetic covariants of a given order and degree in the coefficients; from this law I deduce as a corollary, the law of reciprocity of MM. SYLVESTER and HERMITE. I hope to return to the subject in a subsequent memoir.

X. *On the Functions and Structure of the Rostellum of* Listera ovata.

By J. D. Hooker, *M.D., F.R.S. &c.*

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My attention having been directed by the Rev. Professor Henslow, to a remarkable irritability of the rostellum in a common English orchideous plant, the *Listera ovata*, I have taken the earliest opportunity of following up his observations on the living plant, and of dissecting the organ in question; an account of the anatomy and functions of which I have now the honour of laying before the Royal Society.

The rostellum of *Listera ovata* is a broad, blunt, tongue-shaped organ, terminating the column, and projecting forwards, below the anther, and above the stigma. Soon after the flower opens, if the rostellum be touched or irritated, two white viscid masses are instantaneously protruded,—one from each side of the apex; these coalesce and form a considerable gland-like body, which attaches itself at once to the bases of the pollen-masses, and usually continues firmly to adhere to the apex of the rostellum also.

Such are the effects of artificial irritation; and a careful inspection of a great number of flowers proves, that in a state of nature this glandular secretion secures the impregnation of the plant, by freeing the pollen-masses from the anther-case, and retaining them on the rostellum, where they break up, and the granules falling over the edges of the latter become applied to the stigmatic surface.

The form and position of the labellum seems also to be of considerable importance in this operation. This organ is attached to the base of the column by a rather narrow claw, beyond which it is bent upwards, so that its anterior surface is brought immediately in front of the rostellum. Soon after the flower opens, a viscid fluid is secreted along the mesial line of the labellum, which retains the pollen-masses when these have accidentally become detached from the anther-case previous to the emission of the viscous masses from the rostellum. In some flowers I also found that the viscous masses had been projected with such force from the apex of the rostellum, that they had carried the pollen-masses with themselves beyond that organ, and had alighted on the viscid surface of the labellum, where they were retained by their bases, whilst their apices were brought into contact with the stigma.

The structure of the rostellum in *Listera ovata* is extremely curious, and, as far as I am aware, quite unique in the Order, though it is highly probable that a similar organization will be found in allied species and genera. From its earliest appearance in the young bud (as a simple transversely elongated cellular ridge) to its fully-formed condition, it undergoes no morphological change of any consequence; its development

being uniform till it acquires its broad tongue-shaped form in the mature flower, when it is about $\frac{1}{30}$th of an inch in length and breadth. In this state it is rather concave upon the upper surface, slightly raised along the mesial line, and with somewhat upturned edges and apex. The margins are tolerably thick, and the apex presents a broad central point, with a shallow sinus on either side of it. The substance is extremely soft, white, semi-transparent and pulpy. Both upper and under surfaces are marked with 30 to 40 delicate parallel striæ, which along the mesial line are straight, while those on either side of it converge towards the apex of the rostellum, the marginal ones being conformable in direction with the outline of that organ. Towards the very apex, these parallel lines are crossed by a few transverse bars (indicating their cellular origin), and at the base they rest upon, or gradually pass into, a papillose cellular tissue, which is continuous with the surface of the column. Two darker areolæ are observable at the termination of the rostellum, occupying the shallow sinus on each side the apex; and these indicate the points from which the viscous masses are ejected through the rupture of the tissue of the cavities containing them.

After the discharge of its viscous contents, the rostellum collapses considerably, its apex and margins become deflexed, and the pollen-granules are allowed to fall over on the stigma.

A transverse section of the rostellum shows that it is wholly formed of continuous longitudinal parallel loculi, corresponding in number with the striæ on the surface; these are separated by septa of excessive tenuity and transparency, but of considerable firmness, and these, as well as the walls of the loculi, present no traces of areolation or cellular structure, except towards the apex and base of the rostellum. The loculi are many times longer than broad, and are much less in width than in depth, their diameter between the two surfaces of the rostellum being about $1\frac{1}{2}$ times greater than that between the septa, whence the appearance presented by a transverse section of the whole organ is that of a galvanic trough of 30 to 40 cells.

Owing to the exceedingly pulpy and transparent character of the rostellum, its irritability, and the viscous nature of its contents, I was wholly unable to understand its structure in the living plant, and had recourse to specimens preserved in spirits three years ago by Professor Henslow.

On opening the loculi, each was found to contain a very elongated club-shaped body, conformable in shape to that of the loculus (whose form might hence be deduced from that of its contents). These bodies, which are the viscous secretion of the rostellum in a hardened state, were very much flattened laterally, gradually narrowed upwards into slender points, with somewhat swollen tips, slightly curved and obliquely truncated at the base. Their bases, or rather those of the loculi which contained them, rested upon the loose cellular tissue of the column, which was distended with fluid, chlorophyll and acicular raphides.

In their youngest condition these club-shaped bodies are more opaque, and appear covered with hexagonal areolæ (an indication of their cellular origin), and are com-

posed of a grumous fluid full of minute transparent chlorophyll-globules of various dimensions. As they advance to maturity, the cell-walls disappear, and the whole tissue appears more uniformly grumous; on its first discharge from the rostellum, it presents the appearance of a glairy fluid, charged with transparent granules, acicular raphides, and traces of an hexagonal cellular tissue or rete.

The expulsion of the contents of the loculi is no doubt the natural effect of the distension of the latter, which causes the rupture of the apex of the rostellum at two points. Whether the simultaneous discharge of all the loculi is wholly a mechanical, or in part a vital action, may possibly be doubtful; if the latter, it may present some analogy to the simultaneous protrusion of the tubes from all the pollen-grains forming the pollen-mass of *Asclepias Curassavica*, first indicated by Mr. Brown. In one instance, however, I succeeded in causing the contents of each loculus to be voided separately in vermiform masses, by compressing an immature fresh rostellum in water.

Soon after its emission the viscous mass hardens, becomes reddened, and usually adheres very firmly to the apex of the rostellum. It is not acted upon by iodine beyond being faintly browned.

The membrane of which the walls of the loculi are composed is excessively thin and transparent, and presents a beautiful appearance under the microscope; each line marking the position of the septa being bordered with a band, which is composed of excessively fine, straight, oblique or wavy striæ, which are placed at right angles to the septa.

The position and function of this glandular secretion naturally recall the theory once proposed to explain the impregnation of *Orchideæ*, which assumes that operation to take place in many species of the Order through the glands at the base of the pollen-masses; I therefore sought diligently for any facts that might countenance such a supposition in *Listera*, but in vain. I was unable to detect pollen-tubes in the glandular body at any period; and I repeatedly spread the pollen over the viscous matter when under the microscope, but without any effect; on the other hand, those pollen-grains that were placed on the stigma emitted boyaux abundantly.

In a morphological point of view, the exact nature of this complicated and highly organized rostellum is not very evident; but it may be remarked, that its position would suggest a theoretical relation with the two undeveloped stigmata of the natural order, whose position may be supposed to coincide with that of each half of the rostellum. The blending of the different suppressed organs forming the column of *Listera* is, however, so complete, that in the present state of our knowledge it is perhaps safer to regard this curious organization of the rostellum as an accessory stigmatic organ, or appendage to the stigma, such as those which occur in various natural families of plants, and more or less directly facilitate the office of impregnation.

The relation of these glands to those which congenitally connect the pollen-masses of so many genera of *Orchideæ* (either directly, or indirectly by means of the caudicula) is on the other hand very evident, and the structural passage between them may be traced through those genera in which each pollen-mass has a separate gland developed at its base, in a fovea of the rostellum. Another modification of structure in the rostellum occurs in certain genera allied to *Listera*, in which that organ is described as becoming divided into two arms, through the absorption or falling away of the intervening substance.

In all these cases the special function of the rostellum appears to be the same, and they afford beautiful instances of a great variety of modifications of structure in one organ, being all adapted to the performance of one very simple function, namely the retention of the pollen-masses. With regard to the degree of complexity presented by the several modifications alluded to, it would appear, that, taking *Listera ovata* as an extreme case, a very simple form of pollen here accompanies a very complex organization of rostellum, whereas in some *Vandeæ* which have eight pollinia attached to a strap-shaped caudicula, and that again fixed congenitally by an externally developed viscid gland to the rostellum, the latter is a mere cellular protuberance. Between these remarkably contrasted forms there are very numerous and evidently intermediate grades and modifications of structure, besides a great many which have not hitherto been reduced to any theoretical law of comparative development.

Though I have given here the results of a long and very careful examination of *Listera*, I consider the subject as far from exhausted. Professor Henslow has had the kindness to overlook my dissections and drawings, which will I trust be found tolerably faithful, but there are many minute points in this species which yet require to be carefully investigated, whilst an examination of its allies would doubtless throw much light upon the structure and functions of the many curious forms of the column in *Ophrydeæ*.

PLATE I.

Fig. 1. Flower of *Listera ovata* with the perianth removed, before the protrusion of the gland. *a*, termination of column; *b*, anther-case; *c*, pollen-masses; *d*, rostellum; *e*, stigma; *f*, base of the labellum.

Figs. 2 and 3. Vertical sections of two other flowers of *Listera ovata*, fig. 2 before, and fig. 3 after, the protrusion of the gland, which is shown at *d* of fig. 3. The other letters indicate the same organs as in fig. 1.

Fig. 4. Rostellum seen from above; (*a*) the discoloured spots where the glandular masses are protruded.

Fig. 5. Vertical section of anterior portion of column, through the rostellum (*a*), showing one loculus and its contents (*b*), and stigma (*c*).

Fig. 6. Transverse section of rostellum. *a*, loculi; *b*, their contents *in situ* as coagulated by alcohol.

Fig. 7. Half the rostellum with the striated wall removed. *a*, the contents of the loculi (as coagulated by alcohol); *b*, the broken septa of the loculi.

Fig. 8. Very highly magnified view of the loculi, showing the band of transverse striæ (*a*) bordering the lines indicating the position of the septa.

Fig. 9. Contents of the loculi.

Fig. 10. Upper portion of one of the same, in a very immature state, showing the areolation of its surface.

Fig. 11. Very highly magnified view of the substance of the gland on its first expulsion.

Fig. 12. Pollen-grains.

XI. *An Account of the Organic Chemical Constituents or Immediate Principles of the Excrements of Man and Animals in the Healthy State.* By W. Marcet, *M.D., F.C.S., formerly President of the Edinburgh Medical Society, Corresponding Member of the Société de Biologie of Paris, and Member of the Parisian Medical Society. Communicated by* Francis Marcet, *Esq., F.R.S., Geneva.*

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THE following investigations on the immediate principles which constitute the evacuations of Man and animals were undertaken with the view of endeavouring—

1st. To determine some of the modifications which the unabsorbed part of food undergoes in the alimentary canal.

2nd. To obtain an insight into the nature of the secretions yielded by the glands and mucous membrane of the colon and rectum.

3rd. To extend our pathological knowledge, and afford new means of diagnosis, by applying a method of analysis to healthy human evacuations, thus affording to physicians and pathologists an opportunity of examining these matters in a morbid state.

I had proposed, in the first instance, to confine my researches to healthy human evacuations, but having detected a method of analysis which enabled me to obtain several of their immediate principles in the pure state, I was induced to continue the investigation with reference to the castings of various *carnivorous*, *herbivorous*, and *granivorous* animals. The castings of the Tiger, Leopard, Dog, Crocodile, and Boa were first examined. Then those of the Dog (fed upon bread), Horse, Sheep, Wild Boar, Elephant, and Monkey; and, lastly, the castings of Fowls.

1. *Of the Healthy Human Evacuations.*

The results obtained from the study of the nature and composition of healthy human evacuations, together with the method of investigation employed, have been condensed into a synoptic table annexed to the present communication.

It is superfluous to dwell upon the odour, colour and consistence of human fæces; their reaction is constantly alkaline, and they yield but a very weak extract to distilled water. This alkaline reaction is common to the castings of every animal, and is very probably owing to the presence of ammoniaco-magnesian phosphates, the only strongly alkaline immediate principle which I have obtained from excrements, and which, being soluble, though sparingly, in hot water, is the cause of their alkaline nature.

When boiled in alcohol, human fæces yield an abundant extract, and if small quantities of alcohol be used at a time, and the extract rapidly filtered through a rough, clean cloth, nothing remains on the filter but a brown mass, devoid of smell, insoluble in ether, and yielding to boiling water nothing but ammoniaco-magnesian phosphates, which can be obtained crystallized by slow evaporation.

It was found necessary to operate each time on the whole evacuation, which was treated with boiling alcohol of specific gravity 845: upwards of fifty human evacuations were examined, about a pint and a half of alcohol being required for each operation; the fæces were previously mixed with a little water, to facilitate the action of the alcohol when their consistence was too solid. This alcoholic extract had a very distinct smell of the matter examined, and a strong acid reaction, showing that one or more acid principles exist as constituents of human evacuations. The alcoholic solution was set aside for twenty-four hours, when an abundant deposit was found at the bottom of the beaker; the fluid was decanted, and the deposit collected upon a filter. The alcoholic solution still possessed an acid reaction; it had a slightly viscous consistence, and a dark olive-brown colour. This fluid was treated by a variety of processes, which yielded no satisfactory result, until milk of lime having been added, with the view of precipitating the fatty acids it might contain, as I had done on a previous occasion to obtain the fatty acids of the blood*, a distinct precipitate occurred of a yellowish-brown colour, subsiding after a few minutes, and leaving a clear brown straw-coloured fluid; this precipitate was collected, after an hour or two, upon a filter. It had a viscous nature and a yellowish-brown colour. The filtrate was set aside, and the lime precipitate left to dry upon filtering-paper. When the excess of moisture had thus been removed, and the precipitate obtained had become comparatively dry, it was transferred to a small glass phial, and agitated with ether: in some instances I used boiling ether, but soon found it was unnecessary, so that cold ether was generally employed. The contents of the phial were next filtered, and a clear yellow ethereal solution thus obtained. The lime precipitate was then washed with ether, and the entire solution finally allowed to evaporate spontaneously. After a period varying from one to three days, the fluid was found to contain a quantity of beautiful silky crystals, collected in masses or tufts adhering to the sides and bottom of the beaker, gradually increasing in size and numbers, and throwing out in every direction extremely fine and light ramifications. The mother-liquid having been decanted, and the substance placed upon filtering-paper, the crystals were found to be so fine and delicate as to be crushed by the mere weight of the fluid contained between them, so that, when dry, their crystalline structure had nearly disappeared, the substance having assumed the appearance of light flattened brittle scales. The crystals thus obtained are far from pure, being mixed with an oily yellow matter, which

* Recherches sur la Nature des Graisses qui se trouvent dans le Sang. Bibliothèque Universelle de Genève, 1851.

proves most difficult to remove. By redissolving them, however, in ether, and allowing the solution to evaporate spontaneously, the substance may be obtained comparatively pure, though not always colourless. I have obtained a nearly colourless solution by filtering the fluid through very finely divided animal charcoal. The crystals obtained from this second solution were generally very much larger than in the previous case, especially when a little alcohol had been added to the ether. These crystals, when viewed under the microscope, were seen to consist of acicular four-sided prisms; they were collected upon a filter, dried and preserved.

This constituent of human evacuations, which I propose to call *excretine*, was detected in every case of healthy human fæces examined; it can be obtained very easily by the above process, even from a small sample of excreted matter, and recognized at once by the silky and very light nature of the tufts.

It is very soluble in ether or hot alcohol, but sparingly so in cold alcohol, and does not precipitate or crystallize on cooling; its solution in ether and in alcohol has a decided though weak alkaline reaction; it is insoluble in water, both cold and hot.

When suspended in boiling water, excretine fuses into a yellow resinous mass floating on the fluid. If dissolved in this state in ether, it again crystallizes when the solution is sufficiently concentrated. When treated with water containing any of the mineral acids, no decomposition ensues, even if the fluid be evaporated nearly to dryness; nothing is obtained but the above resinous mass, which again yields crystals of excretine when dissolved in ether; excretine does not therefore apparently combine with mineral acids. When heated upon a platina knife, the crystals first fuse, evolving a peculiar aromatic smell; they afterwards burn with a slight flame, disappearing very rapidly, and leaving a brown stain, which, on the further application of heat, is completely removed, and no inorganic residue is left behind. The fusing-point of excretine was constantly found to be between 95° and 96° Centigrade.

If excretine be boiled for several hours in a solution of potash, no saponification takes place; the fused crystals float on the fluid, and if dissolved in ether, the substance can again be obtained crystallized.

The elementary quantitative analysis of excretine and the products of its decomposition will constitute the subject of a future inquiry. With respect to its qualitative composition, I have detected *sulphur* as one of its constituents, by calcining a sample of well crystallized and perfectly white excretine with a mixture of carbonate of soda and potash previously ascertained to contain no sulphuric acid. The calcined mass having been dissolved in water acidulated with pure nitric acid, the addition of chloride of barium caused a distinct precipitate. I have also ascertained, by the method of Will and Varrentrapp, that excretine contains a small quantity of nitrogen.

I have not yet investigated the products of decomposition of excretine, but if nitric acid be added to a hot solution of this substance in alcohol, a brisk action

ensues, nitrous acid fumes are evolved, and by concentrating the fluid on the water-bath, another substance is obtained, under the form of beautiful colourless crystals shooting from one side of the capsule to the other, and presently filling up the whole space the fluid occupied. This substance has a strong acid reaction, and is very soluble in water; it attracts rapidly moisture from the atmosphere and deliquesces. However, although it may be interesting in a chemical point of view, as it is not a constituent of excrements, I shall not dwell any longer for the present upon its properties.

It was a matter of considerable importance to ascertain in what form excretine exists as a constituent of human fæces, and if this substance is one of their immediate principles. I have scarcely any doubt as to the greater proportion of excretine existing in the free state as a constituent of excrements, and therefore constituting, in that form, one of their immediate principles, as in several cases I have observed excretine crystallize directly in the alcoholic extract of fæces before the addition of lime. Moreover, although the lime precipitate generally yields, besides this substance, an organic acid which I have found to be margaric acid, it is hardly possible to suppose that lime could have the property of so rapidly decomposing a combination of margaric acid with excretine, should such a compound really exist. I have also ascertained by direct experiment, that if lime be added to a solution of margaric acid and excretine in alcohol, both are precipitated, the margaric acid combining with the lime, and the excretine adhering mechanically to the precipitate formed. It may consequently be assumed that the greater proportion, if not the whole of the excretine contained in human fæces, exists in the uncombined state, or as one of their immediate principles.

Nothing positive is yet known in regard to the mode of formation of excretine in the human body. It may, however, be surmised that it is dependent in some degree on the nature of the alimentation; at least I have noticed an excess of excretine when a considerable amount of beef had been taken, and, on the other hand, a smaller amount than usual of that substance was obtained in a case of diarrhœa attended with loss of appetite. Age and temperament do not appear to modify the production of excretine.

In order to determine the source or mode of formation of excretine in the human body, and complete its physiological history, it will be necessary to ascertain—

1st. Whether it exists in animal food or muscular tissue.

2nd. In what part of the intestines it is first to be detected.

3rd. Whether it can be found in any other part of the human body.

4th. Whether it exists in the castings of animals.

1st. With the view of ascertaining whether animal food or muscular tissue contained excretine, a sample of fresh beef, free from fat, was carefully minced, and treated with boiling alcohol; a colourless extract was obtained, which being filtered through calico, and allowed to stand for some hours, yielded but a very scanty

deposit. Milk of lime produced in this extract a white precipitate, which was collected upon a filter and treated with ether. After twenty-four hours this ether gave by spontaneous evaporation small round translucid masses adhering to the sides and bottom of the beaker, which, when examined under the microscope, were found to consist of round groups of crystals radiating from a centre, and so densely crowded that they could not be distinctly seen unless previously crushed. Small dark specks were mixed here and there with the crystals, but no globules of oil were perceptible, although the evaporation of the ether was nearly complete. When pressed between folds of filtering-paper, the substance left an oily stain; if heated on a platina knife, it immediately fused, and burnt with a gentle flame, evolving a smell of burnt fat. No inorganic residue remained on the platina knife after incineration. The crystals polarized light readily and beautifully; when allowed to dry upon the slip of glass placed under the microscope, they completely lost their distinct structure. No further examination of this substance was attempted, but the characters above-mentioned are sufficient to show, that though in some respects not unlike excretine, it differs from that substance by its fatty nature, and may safely be considered as *stearine*, which it was natural to find in the sample of beef examined.

2nd. The difficulty of obtaining the contents of the human small intestines in the healthy state is so great, that I have not yet been able to ascertain satisfactorily whether excretine be present or not in that part of the alimentary canal; I could not however succeed in obtaining it from the contents of the small intestines of a man who had died from disease of the heart. In this case the alcoholic extract had a pale brown colour and an alkaline reaction; milk of lime added to it gave a precipitate of a light yellow colour, which on being treated with ether, yielded after four days a white amorphous deposit, but no crystals of excretine could be detected.

3rd. With a view of ascertaining whether excretine was to be found in other parts of the body, the parenchyma of the human spleen was next examined. The first spleen which came under my notice was that of a patient of St. George's Hospital who had died from fever; it was apparently healthy; about a quarter of the organ was washed, minced, and boiled with alcohol; the extract yielded on cooling but a scanty deposit. Lime-water having been added, a precipitate was formed, which was collected upon a filter, and subsequently treated with ether, the solution yielding after two days by spontaneous evaporation a number of shining crystals, which, when examined under the microscope, presented the exact appearance of cholesterine. Two other samples of the tissue of the spleen were examined; the first was obtained in a case where death had occurred from an obstruction of the pyloric orifice of the stomach; the second was extracted from the body of an old woman who had died from ascites, accompanied by malignant disease of the ovaries and uterus; this spleen was congested, very friable, and coarsely granulated. In both cases I obtained the same crystalline substance as in my first experiment. It was

found to have the following properties. When obtained directly from its solution in ether, the crystals consist of large, rectangular plates, which, when viewed with the naked eye, floating in the mother-liquor, have the appearance of light shining crystals with a pearly or silky lustre. When collected upon a filter, they rapidly lose their shining nature, which is not the case with cholesterine. Like cholesterine, however, they are insoluble, or very sparingly soluble in cold alcohol, but dissolve readily in hot alcohol, from whence the substance again crystallizes on cooling. The crystals thus obtained still possess the same silky shining lustre as in the previous case, but when subjected to the microscope are found to have lost their rectangular shape, and to have assumed various irregular forms, resembling flies or butterflies with extended wings; they still polarize light very readily. If a few of them be dissolved in a comparatively large amount of alcohol, the substance assumes, on crystallizing, remarkably curious and beautiful forms. Its alcoholic solution has a slightly alkaline reaction; its fusing-point is very high, above 100° Centigrade.

The substance just described cannot possibly be mistaken for excretine, and I should be inclined to consider it as a new immediate principle, unless further investigation should show its complete analogy with cholesterine. It must at all events act an important part in the functions of the spleen, from its having been ascertained to exist as one of the immediate principles of this organ in every case where the spleen was subjected to examination.

Among the intestinal secretions, I have only examined bile (oxen's bile), which yielded no excretine, but only cholesterine, from which circumstance it may be inferred that the method employed for obtaining excretine may also be made use of with advantage to extract cholesterine from its solutions. Indeed, bile contains so small a quantity of cholesterine, that this principle cannot easily be obtained by the usual method, except by operating upon a very large quantity of fluid.

Excretine was not detected in healthy human urine treated by the same method; the lime precipitate, carefully washed with water in order to separate every trace of urea, yielded no perceptible extract to ether.

Blood, human bile, the cerebral and osseous tissue, pancreatic juice, saliva, gastric juice, &c., have not yet been examined in order to ascertain whether they contain excretine. If further experiment shows that this substance can be obtained in no other case than in that of the intestinal evacuations, its formation must evidently result from a metamorphosis or decomposition owing to the action of the solid ingesta upon the intestinal secretions.

From the singular circumstance that excretine contains sulphur, it is not unlikely that the formation of this immediate principle may depend upon a decomposition of taurine, the only sulphuretted compound which, with the exception perhaps of a very small quantity of cystine, can be obtained from the intestinal secretions. Another and very important conclusion resulting from the presence of sulphur in excretine, is, that sulphur is thus eliminated from the body without undergoing

oxidation. The sulphur contained in the body is therefore evidently not all oxidized, and it is not impossible that a large proportion of the sulphur existing in the organic compounds of the body may by this means be eliminated from the animal economy.

The precipitate obtained by the addition of milk of lime to the alcoholic extract of human evacuations having been thoroughly washed with ether in order to separate the whole of the excretine, still generally yields to water or alcohol, when treated with hydrochloric acid, a fatty substance having an acid reaction. The characters of this substance, evidently an important constituent of the human evacuations, are precisely those of margaric acid; by combining with the lime added to the alcoholic extract, it is precipitated along with the excretine and colouring matter. To obtain it, two methods may be employed:—1st. The lime precipitate, deprived of its excretine, is mixed with alcohol, and heated on the water-bath with hydrochloric acid until the whole is dissolved. The acid fluid, on cooling, deposits a mass of crystals, which are collected upon a filter; the filtrate containing the colouring matter, which is set free by the action of the acid, has now assumed a dark red appearance. 2nd. The lime precipitate, deprived of its excretine, is suspended in water and decomposed by hydrochloric acid, with the aid of a gentle heat. By this means it is converted into chloride of calcium, and the insoluble fatty acid being set free is found floating in the liquid. Thus obtained, it has a dirty red colour, and no crystalline appearance; it is next collected upon a filter, and dissolved in hot alcohol; still it does not crystallize on cooling; but if a small quantity of water be added to the solution until a muddiness be induced, and heat again applied, the alcohol on cooling will deposit a crystalline substance identical with that obtained by the former process. If an excess of water be added, with the application of heat, this same substance is deposited in an amorphous form, but may be again obtained crystallized by the same process.

The fatty acid obtained from the lime precipitate was found to have the following properties:—It is soluble in ether and in hot alcohol, but insoluble in cold alcohol; its solution has a distinct acid reaction. When dissolved in hot alcohol, it does not precipitate or crystallize on cooling. It is entirely insoluble in water, and precipitated if water be added to its alcoholic solution; by heating the mixture the precipitate redissolves, and crystallizes on cooling. In its crystalline state it is colourless, has a light consistence and a pearly lustre; the crystals cannot be distinguished by the naked eye, but when examined with a microscope, they exhibit the peculiar structure of margaric acid; some have an arborescent appearance, while others consist of round masses of crystals radiating from the centre, their peripheral extremities being curved in a peculiar manner, and bearing a striking resemblance to margaric acid. If exposed for some time to the air, suspended in water, or in a mixture of water and alcohol, their structure becomes indistinct. When heated upon a platina knife they fuse, evolve a peculiar smell and thick fumes which burn with a flame, and a

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dark stain is left on the previously polished platina; this stain finally disappears, leaving no residue. They were found to be capable of combining with hydrated oxide of lead, the compound being insoluble in ether. The salt of lead, previously washed with ether in order to remove the oleate of lead, should any be present, and then decomposed by sulphuric acid, yielded to the ether an acid solution, which, after being thoroughly washed with water in order to separate the free sulphuric acid, and then evaporated spontaneously, deposited a colourless crystalline substance. This substance was dried under the air-pump over sulphuric acid, then fused on the water-bath and introduced into a capillary tube, when on cooling it again assumed the crystalline state. Its fusing-point was found to be 52° Centigrade, a temperature inferior, it is true, to that of 60° required for the fusion of margaric acid; the difference I believe to be owing to a trace of oleic acid, which remained mixed with the crystals. The small quantity of the substance left after the above manipulation, prevented me from having recourse to repeated crystallizations, the only process by which the fatty acids can be obtained perfectly pure.

The characters of the fatty acid which I have just described so completely agree with those of margaric acid, that no doubt remains in my mind as to the complete identity of the two substances *.

As an additional proof of its presence, a sample of pure margaric acid, which I happened to have prepared on a previous occasion, was dissolved in hot alcohol and lime-water added to the solution, a compound of lime and margaric acid precipitated and was collected upon a filter; the precipitate, suspended in alcohol, was decomposed and dissolved by hydrochloric acid, aided by the application of heat, and on cooling, the margaric acid was obtained crystallized. I afterwards ascertained that margaric acid was endowed with the singular property of crystallizing from its solution in alcohol, when the liquid is heated with just enough water to make it become turbid when cold. This circumstance is also a proof that the above fatty acid obtained from human evacuations is not stearic acid, as a sample of pure stearic acid treated by the same process could not be made to crystallize. The solution retained its muddy appearance, the addition of a large amount of water causing an amorphous indistinct precipitate.

It is not possible to state whether a small quantity of the margaric acid obtained by the above process does not exist in the form of a compound as a constituent of human fæces, but from the very acid reaction of the alcoholic extract of excrements, it appears most probable that the whole of this fatty acid exists in the free state in human fæces as one of their immediate principles. I hope, at all events, to have proved satisfactorily that margaric acid is to be found, though not constantly, in the human fæces; and from the circumstance of my never having detected margarine as one of their constituents, I may be allowed to conclude that a process similar

* According to Lehmann, margaric acid has occasionally been detected in solid excrements by means of the microscope.—Physiological Chemistry, vi. p. 108.

to saponification takes place in the intestinal canal, together with the further decomposition of the soap into its acid and base. According to Cl. Bernard, the above saponification occurs in the duodenum by the action of the pancreatic juice, which converts the neutral fats of the food into an emulsion or state fit to be absorbed by the lacteals. If it be considered, moreover, that blood contains free fatty acids, a circumstance first shown by Lecanu, and which I have had myself an opportunity of verifying in Messrs. Wurtz and Verdeil's laboratory at Paris, perhaps we are entitled to admit that the saponification arising from the action of the pancreatic juice upon the neutral fats of food, and the decomposition of the soap, both take place in the duodenum, the excess of free fatty acid which escapes absorption being carried through the intestinal canal, and expelled with the evacuations. If a powerful free acid were found to exist in the blood, it might be supposed that the fatty matters saponified by the pancreatic juice are absorbed, the soap decomposed in the circulation, and the excess of free acid which could not be assimilated, conveyed into the intestines by the intestinal secretions; but as the blood contains no powerful free acid, being, on the contrary, constantly alkaline, this theory cannot be maintained.

I have not yet been able to ascertain with any degree of certainty whether stearic acid be present or not in human evacuations; but if it be considered that margaric acid is habitually found in them, and sometimes even in large quantities, although the fats contained in the mutton and beef taken as food were nearly pure stearine, and if the transformation of stearic acid into margaric acid must take place somewhere in the body, human fat consisting mainly of margarine, are we not entitled to conclude that this stearine is converted into margaric acid during its passage through the intestinal canal?

The third substance present in human excrements, which may be obtained from the lime precipitate, is the *colouring matter*. If this precipitate, deprived of its excretine, be dissolved in alcohol with hydrochloric acid, a dark port-wine-coloured solution is produced, which on cooling deposits margaric acid; the filtrate contains the colouring matter free from this acid. By adding water to the solution, and concentrating it on the water-bath, the colouring matter separates in the form of flakes floating on the fluid, and leaving a nearly colourless mother-liquor. The substance is now collected on a filter, dissolved with hot ether, and the solution washed with water in order to remove the last traces of hydrochloric acid. The ethereal solution, mixed with water and allowed to evaporate spontaneously, deposits the colouring matter in the form of a dark brown or black amorphous substance, exactly similar to the colouring matter extracted by Dr. Verdeil from the blood, and to that which Dr. Harley has lately obtained from urine, with which it appears identical.

I have already alluded more than once to a precipitate or deposit occurring in the alcoholic extract of healthy human evacuations, which appears to be of a very com-

plex nature. If the above alcoholic extract after having stood for twenty-four hours be decanted, and the precipitate collected at the bottom of the beaker thrown upon a filter, the deposit presents an olive-brown appearance, a strongly acid reaction, and the fœtid smell peculiar to fæces. When viewed under the microscope, it appears to consist principally of small oily globules, of a yellow-green colour, having a strong refracting power, and mixed sometimes with crystals of excretine accompanied by a yellow amorphous deposit. This deposit invariably occurred in every healthy human evacuation that I examined. After a few hours, it had assumed a gelatinous consistence; if it was then boiled with alcohol in a capsule or a glass flask as long as it yielded anything to that fluid, and finally filtered through white calico, a substance was left behind, insoluble in boiling alcohol. This substance, when heated upon a platina knife, first fuses, then burns with a flame evolving an oily smell, and leaves a residue of white ashes. The alcoholic filtrate from the above substance, after having been allowed to stand for twenty-four hours, yielded a deposit which fell to the bottom of the beaker; the whole was next thrown upon a filter, thoroughly washed with cold alcohol, and the washings together with the filtrate concentrated on the water-bath. The solid substance remaining on the filter was then washed with ether and yielded an ethereal solution of a yellow colour and very acid. The residue was of a light yellow colour, and, when viewed under the microscope, appeared to consist of an amorphous mass free from globules; dried on filtering-paper, it became nearly colourless and of a light friable nature. When heated on a platina knife, it first fused and assumed a dark colour, emitting a smell of burning oil; it afterwards burnt with a bright fuliginous flame, and finally left a residue of porous white ashes, consisting of phosphate of potash. It did not dissolve in boiling water, but fused and floated on the surface; it was also insoluble in cold alcohol, and when suspended in that liquid sunk very slowly to the bottom, appearing to have nearly the same specific gravity. It is soluble in boiling alcohol, and on cooling is again precipitated. It is very sparingly soluble in cold ether, but becomes more so when heat is applied.

I have not yet sufficiently examined the properties of this substance to be able to determine whether it is a pure immediate principle; indeed, from my having failed in my endeavours to obtain it crystallized, it might be regarded as a mixture of several principles. The above-mentioned properties, however, are distinctly defined, and under all these circumstances, I am inclined to consider it as a combination of phosphate of potash and a purely organic substance.

The ethereal extract obtained from the above substance deposits by spontaneous evaporation a crystalline matter, which has not yet been obtained in sufficient quantity to admit of its being examined.

The clear cold alcoholic solution obtained from the olive-coloured acid deposit, or the filtrate from the substance just described, having been evaporated down on the water-bath, yielded a deep olive-coloured oil, quite fluid when warm, and emitting

the smell peculiar to fresh evacuations. With the view of obtaining it pure, I first dissolve it in ether, in order to remove a solid granular substance of a light consistence, insoluble in ether and in cold alcohol, but dissolving readily in hot, and forming a solution which yields, when concentrated, a number of round globules. These when heated upon the platina knife, fuse, and then burn, evolving a smell of burnt meat, and leaving behind a residue difficult to incinerate; but not having succeeded in obtaining this substance in a crystallized state, I cannot say more at present as to its properties. The oil deprived of the above granular substance, and dissolved in ether, was mixed with alcohol, and subsequently lime-water was added; the mixture was then heated upon the water-bath, until a heavy precipitate, consisting of a compound of this oil with lime, had been deposited. This precipitate was collected upon a filter, thoroughly washed with hot and cold alcohol, and the filtrate set aside. The insoluble salt of lime obtained was now decomposed with sulphuric acid, and treated with ether, in order to separate its organic constituent. The ethereal solution was then well washed with water, to get rid of the sulphuric acid it contained, and when evaporated down on the water-bath, yielded a pure fatty substance having a constant fusing-point. This substance, dried over sulphuric acid at the temperature of the atmosphere, is solid, but fuses invariably between 25° and 26° Centigrade, showing it to exist in a pure state. When heated on a platina spatula, it first fuses, evolving a smell somewhat resembling that of excretine; it next takes fire and burns with a bright flame, which disappears as soon as the platina foil is removed from the lamp; a black stain remains, which, by further application of heat, is completely removed. When boiled with a solution of caustic potash, the substance does not dissolve, but floats on the surface of the liquid. It is insoluble in water, but very soluble in ether, sparingly so in cold alcohol, but dissolving readily in hot, and not precipitating on cooling. Its solution possesses a marked acid reaction.

It is not easy to determine whether this chemical compound, which I propose to name *Excretoleic acid*, is, or is not an immediate principle of human fæces. I am inclined to believe that it exists in them as an acid salt, the base being excretine, or a substance whose properties exactly resemble those of excretine, except that it fuses apparently at a lower temperature. This base is obtained in the filtrate from the precipitate which occurred when milk of lime was used to purify excretoleic acid. I have several times found the filtrate, after twenty-four hours, full of a crystalline mass, which, viewed under the microscope, resembled excretine, possessing the same properties of solubility in alcohol, ether, &c., but fusing at a lower temperature, between 70° and 80°, very probably because I had not obtained it in a perfectly pure state. When this substance was not found crystallized in the alcoholic filtrate, it was obtained by evaporating the solution to dryness and taking up the residue with ether, when it crystallized by spontaneous evaporation.

We have already seen that the addition of milk of lime to the clear cold alcoholic

extract of fæces had caused the formation of the precipitate which has been described as composed of *excretine*, *margaric acid*, *colouring matter*, and *lime*. The filtrate from this precipitate having been concentrated on the water-bath, a scanty amorphous deposit occurred floating in the solution, which, when viewed under the microscope, showed no crystalline structure. The concentrated fluid allowed to stand for several days, yielded no crystals, but merely an amorphous residue. By distilling it with water in a small retort, a few drops of sulphuric acid having previously been added, I obtained a colourless acid fluid, having a strong smell, resembling that of butyric acid, which I at first considered to be owing to the presence of that substance; but on treating this fluid with lime or baryta, I failed to obtain any crystallized salt, showing that butyric acid was not present, and consequently it cannot be considered as a constituent of human evacuations. The alcoholic extract concentrated on the water-bath was also treated with ether; the ethereal solution obtained, decanted and allowed to evaporate spontaneously, yielded on several occasions crystals of excretine.

From the above investigations, I may conclude that human evacuations in the healthy condition contain:

1st. A new organic immediate principle, having a crystalline structure and an alkaline reaction, which I propose calling *Excretine*.

2nd. A substance possessing the characters of margaric acid, which, though not constantly present in human evacuations, is generally found as one of its constituents.

3rd. A colouring matter analogous to that of blood.

4th. A pure olive-coloured fatty acid, which I propose to call *Excretoleic acid*.

5th. Volatile fatty acids, free, however, from butyric acid.

I shall now endeavour to relate as briefly as possible the circumstances and results which attended the examination of the castings of various animals, the method of analysis which I employed being similar to that already followed for the investigation of human evacuations.

2. *Castings of Carnivorous Animals.*

1st. *Castings of the Tiger.*—Newly-passed Tiger's excrements, obtained from the Zoological Gardens in small lumps, were of a pale colour, had a peculiar nauseous smell, and an alkaline reaction. Having previously been washed with a small quantity of water, they were boiled with alcohol, and yielded a pale-coloured alcoholic extract. The solution, left undisturbed for twenty-four hours, gave no deposit, its reaction was slightly acid; milk of lime added to the extract produced a nearly white precipitate, which, after having been dried upon filtering-paper, was treated with ether, both hot and cold, until nothing more could be separated from it. The

ethereal solution, allowed to evaporate spontaneously, was, after three days, found to contain a quantity of shining crystals, polarizing light under the microscope, and mixed with traces of a red amorphous deposit. The crystalline mass, dried first upon bibulous paper and then under the air-pump, assumed the form of slightly brick-coloured translucent scales. When heated upon a platina knife, they first fused, emitting the peculiar smell of the tiger's den, and when allowed to cool exhibited a yellow waxy appearance, reflecting light powerfully under the microscope, but without any crystalline structure. They burnt with a bright flame, leaving traces of a white inorganic residue, probably from their not being quite pure, and hardly any black stain.

The above substance is insoluble or very sparingly soluble in cold alcohol, but dissolved readily in that fluid when boiling. By concentrating the alcoholic solution on the water-bath, arborescent crystals were obtained which dissolved in cold ether, but not so readily as excretine, and again crystallized if the solution was allowed to evaporate spontaneously. These crystals are very similar to those obtained from the alcoholic solution, but appear to lose their structure more rapidly as the ether evaporates than they do when produced from the evaporation of alcohol.

I am not disposed to consider the above substance, which appears to exist in the castings of all the carnivorous animals I have had an opportunity of examining, as identical with human excretine, which it resembles, however, in many of its properties. It appears to differ from it, first, by the shape of its crystals; secondly, by the smell it emits when burnt; thirdly, by a much less degree of solubility in alcohol and ether.

The filtrate from the lime precipitate was concentrated upon the water-bath, when a whitish-pink sediment was deposited, which, when examined under the microscope, was found entirely composed of small round crystalline masses radiating from a centre. The crystals, collected on a filter and dried, burnt on the platina knife with a bright fuliginous flame, and left a white residue, consisting of lime. This salt of lime was found to be soluble, though not very readily, in alcohol; on adding a few drops of water to the solution it turned milky, and on cooling the whole mass instantly crystallized. The addition of sulphuric acid immediately brought out a strong smell of butyric acid; the salt obtained from this alcoholic extract was therefore evidently *butyrate of lime*. It could not be the lactate, although its crystalline form is similar, as the lactate is exceedingly soluble in water, and can only be made to crystallize in a very concentrated solution, contrary to what took place with the substance obtained from the Tiger, which begins crystallizing long before the solution has attained a high degree of concentration.

I was not able to ascertain whether butyric acid exists in the free state, or combined with a base, as an immediate principle of the castings of the Tiger. It is probable, considering the slight degree of acid reaction shown by the alcoholic extract, that this acid occurs in the form of a salt.

2nd. *Castings of a Dog fed upon meat.*—Fresh castings from a Dog, fed in my laboratory for several months upon meat alone, were next examined. They had an alkaline reaction and a dark brown colour. When washed with a little water and boiled with alcohol, they yielded an alcoholic solution, of a red colour when seen by reflected light and possessed of a slightly acid reaction. Put aside in a beaker for twenty-four hours, very little or no deposit occurred. The extract was mixed with lime-water, which caused the formation of a very light yellow precipitate. I treated it with ether, as in the previous cases, and allowed the ethereal solution to evaporate spontaneously. After four days, a shining crystalline deposit was observed floating in the liquid, which exactly resembled the substance obtained under similar circumstances from the castings of the Tiger. The filtrate from the lime precipitate having been concentrated on the water-bath, was soon observed to be full of crystals floating in the fluid in the form of white masses. When viewed with the microscope, they were found to be elongated prisms irregularly grouped in large masses. Heated upon a platina knife, they burnt with a flame, and left an ashy residue composed of lime. When a drop of sulphuric acid was added to some of the crystals dried on filtering-paper, and heat subsequently applied, a distinct smell of rancid butter, peculiar to butyric acid, was evolved, showing them to be butyrate of lime. After some days, the solution of the salt in alcohol, previously filtered through animal charcoal to remove the colouring matter, yielded by spontaneous concentration a number of perfectly white globular masses of crystals about the size of a large pin's head, which, when dried upon filtering-paper, assumed a beautiful silky appearance. In conclusion, the castings of dogs fed upon meat contain butyric acid, but whether it be in the form of a free acid or of a salt, I have not yet satisfactorily ascertained.

Crocodile's Excrements.—During a visit to the Zoological Gardens, I had an opportunity of obtaining from the crocodile's cage a small quantity of the fresh castings of this animal. They had a peculiar fœtid smell, and when dried could be easily pounded into a white powder, some of which, treated with nitric acid and ammonia, failed to denote the presence of uric acid. The pounded mass, after having been converted into a paste with a few drops of distilled water, and then boiled with alcohol in a glass flask, was thrown upon a calico filter. The filtrate having been a few hours afterwards mixed with lime, a yellow precipitate was thus produced; this precipitate was subsequently filtered and boiled with ether. The filtered ether, left to spontaneous evaporation for a day and a night, yielded a large quantity of broad silky crystals floating in the liquor, which when viewed through a microscope, were found to have exactly the form of *cholesterine*. Heated upon a platina knife, the substance fused and burned with a brilliant flame, like cholesterine, leaving no residue. It had also a light consistence and the pearly lustre of cholesterine, was insoluble in water and in cold alcohol, but soluble in hot alcohol. From the above results, there is every reason to believe that this substance is cholesterine: this immediate principle of the bile is known, moreover, to exist generally

in the castings of hibernating animals. I am not, however, aware whether it has been as yet extracted from those of the Crocodile.

The occurrence of cholesterine in the excrements of the Crocodile, and not in those of the Boa or any other animal which I have examined, is a phenomenon worthy of notice. It may be concluded from it, that a portion only of the bile secreted by the Crocodile is modified or absorbed during digestion, and the rest eliminated with the casting.

Boa.—I treated the castings of the Boa in the same way as those of the Crocodile, but without finding cholesterine. It has already been observed that the above method was applied to the examination of bile, and that cholesterine was obtained; so that had any cholesterine been present in these castings, it could not have escaped observation.

Leopard.—The castings of the Leopard were also examined; the lime precipitate in the alcoholic extract having been treated with ether, and the ether allowed to evaporate spontaneously, yielded a mass of light colourless crystals, readily reflecting light, and resembling those obtained in similar circumstances from the Dog and Tiger, but not mixed with the red amorphous substance.

In conclusion, the castings of the carnivorous mammalia appear to contain the peculiar light crystalline substance, differing in its properties from excretine, and obtained from the ethereal extract of the lime precipitate above described. I have constantly failed to detect excretine as a constituent of these castings.

The excrements of the carnivorous mammalia also contain butyric acid, or some of its salts, while in no case have I been able to obtain this substance from human fæces, where it was thought to exist. There is probably, therefore, some chemical change going on in the intestines of these animals different from what occurs in the human alimentary canal, and the butyric acid, unless it be secreted from the mucous membrane of the intestines, must result from some change which the animal food undergoes in the intestine during the process of digestion. It is not impossible that some of the sugar elaborated by the liver may be converted into butyric acid in the circulation and eliminated through the intestines.

The fæces of the Crocodile and Boa materially differ from each other, the former containing cholesterine, but no uric acid, and the latter being nearly entirely composed of urates, but containing no cholesterine. The rule applied to hibernating animals meets here with an exception; further investigation is therefore necessary before any positive and general law can be arrived at.

3. *Of the Castings of Herbivorous Animals.*

The castings of the *Horse*, *Sheep*, *Dog fed upon bread*, *Wild Boar*, *Elephant*, and *Monkey* were next examined: in no case could I succeed in detecting the presence of excretine or of butyric acid as one of their constituents.

The following are the peculiarities which the examination of those excrements presented:—

Castings of the Horse.—Horse's excrements, boiled with alcohol, yielded but a very scanty deposit on cooling; but the solution, mixed with milk of lime, gave a yellow precipitate of a light homogeneous nature. The ethereal extract from this precipitate, evaporated spontaneously for twenty-four hours, left a yellow residue viewed under the microscope as drops of oil; but not a trace of excretine could be detected. The filtrate from the lime precipitate, concentrated on the water-bath, did not yield any butyrate of lime.

Castings of the Sheep.—Newly-passed castings of the Sheep, washed with a little alcohol and boiled in that liquid, gave a deep green extract, in which milk of lime produced a very abundant green precipitate, the liquid remaining yellow. Thi precipitate, collected on a filter and treated with ether, yielded a dirty dark green solution, which, allowed to evaporate spontaneously, deposited after twenty-four hours a green mass, observed under the microscope to consist of an amorphous and a crystalline substance. The latter, though not distinctly defined, possessed a yellow colour, refracted light very readily, and polarized. No substance resembling excretine was obtained. From the difficulty of separating the above crystalline substance from the green amorphous matter, the investigations on this part of the subject are necessarily imperfect.

The filtrate from the lime precipitate did not yield any butyrate when concentrated.

Castings of a Dog fed upon bread.—The castings of a Dog fed for about a month upon nothing but bread gave a very pale alcoholic extract, yielding but a slight deposit on cooling. The precipitate produced by the addition of lime to this extract was of a yellow colour, and when treated with ether, prismatic crystals were obtained by its spontaneous evaporation, usually grouped three or four together, meeting at one extremity and diverging at the other. Some groups had a less defined character, and resembled leaves converging at one of their extremities; they polarized light beautifully. These same crystals were obtained in one instance from the castings of a dog fed upon meat, of which they are probably merely a modification.

Castings of the Boar.—Fæces from the Wild Boar were procured fresh from the Zoological Gardens, the animal being fed upon biscuit and cabbages. These castings occurred in the form of green masses, having an alkaline reaction. When washed with a little water and boiled in alcohol, they yielded a dark green solution. An abundant deposit occurred on cooling, from which the fluid was decanted. Milk of lime added to the solution produced a yellow precipitate, as in the previous cases. It was treated with ether, which was allowed to evaporate spontaneously. After a week a green deposit was obtained, composed of an amorphous green oil and arborescent crystals, readily polarizing light; they had not, however, the peculiar look of excretine, and did not crystallize in tufts like that substance. The filtrate

from the lime precipitate, concentrated on the water-bath, left a green residue having an oily consistence. Ether being added, dissolved this green substance, which was again deposited by spontaneous evaporation, without assuming a crystalline form. No butyric acid was therefore present.

Castings of the Elephant.—I obtained from the Zoological Gardens a sample of the castings of an Elephant fed with cabbage, hay, oats, and chaff; they occurred in large masses, their consistence resembling that of horses' excrement. When washed with a little water and boiled in alcohol, they afforded an alcoholic extract, which on cooling yielded an olive-coloured deposit. The precipitate obtained by adding lime to the alcoholic solution decanted from the deposit, was of a yellow-brown colour. It was treated with ether, which, after having stood undisturbed for three days, yielded a bulky deposit, presenting no distinct structure when viewed under the microscope. The examination of these castings presented the following peculiarities, which I must not omit noticing. The ether with which the lime precipitate had been boiled having been decanted, deposited, on cooling, a white gelatinous substance, insoluble in cold ether and in alcohol, but which dissolved immediately on the addition of a few drops of hydrochloric acid to the alcohol, and the application of a gentle heat; it again solidified on cooling, giving the whole fluid a semi-solid appearance. Examined with the microscope, it appeared composed of amorphous transparent masses. Pressed between folds of bibulous paper, it assumed a pure pearly aspect, very similar to that of margaric acid. If heated, it fuses very readily, emitting scarcely any perceptible smell, burning with a slight blue flame, and leaving behind a black stain, which, by the further application of heat, completely disappeared, nothing remaining on the spatula.

From the preceding experiments, it appears probable that the substance I have just described is a pure constituent of the Elephant's castings.

Castings of the Monkey.—I treated with boiling alcohol a sample of the castings of the Monkey, obtained from the Zoological Gardens, but could not detect the presence of excretine as one of their constituents. The lime precipitate obtained from the Chimpanzee's excrements, treated with ether, and the ether left to evaporate spontaneously, yielded crystals polarizing under the microscope, and very much resembling in structure those obtained by the same process from the Tiger.

4. *Castings of Granivorous Animals.*

The only castings of granivorous animals I had an opportunity of examining were those of fowls fed with oats. In this case also I could obtain no excretine. The castings boiled with alcohol left an insoluble mass entirely composed of oat-husks; the yellow alcoholic solution, mixed with milk of lime, deposited a yellow precipitate, which yielded to ether a faint yellow solution. After spontaneous evaporation for two days, the ether was observed to deposit an amorphous yellow sediment, which, viewed under the microscope, was found to consist of a mass of

transparent globules, resembling exactly those obtained by the same process from the castings of the Horse. No crystals were deposited by the ethereal solution.

My investigations upon the chemical constituents of the castings of animals show, therefore,—

1st. That they contain no excretine, thus differing very materially from human evacuations.

2nd. That the castings of carnivorous mammalia contain,—(1) a peculiar crystalline organic substance obtained by the same process as excretine; (2) *butyric acid*, existing probably in the form of a salt, as one of their constituents.

3rd. That the castings of the Crocodile yield *cholesterine*.

4th. That the castings of herbivorous animals contain no excretine and no butyric acid, and do not yield the crystalline substance obtained from those of carnivorous animals, except perhaps in the case of the Monkey.

Synoptic Table of the Immediate Principles of Human Evacuations in the Healthy State.

- **Fæces boiled with alcohol.**
  - Substance insoluble in alcohol, consisting of ammoniaco-magnesian phosphate, other inorganic salts, organic fibres, and other parts of food which have escaped absorption.
  - Substance soluble in boiling alcoholic extract, but subsiding as soon as the fluid has become cold. When collected upon a filter and boiled in alcohol, it yields
    - A substance insoluble in boiling alcohol.
    - A substance soluble in boiling alcohol, but precipitating on cooling, which, when washed with ether, yields
      - A pure non-crystallizable substance, soluble in hot alcohol, but precipitating in the solution when cold; not yet sufficiently examined to rank as an immediate principle.
      - A substance soluble in ether, and crystallizing by spontaneous evaporation.
    - A substance soluble in boiling alcohol, and not subsiding in the cold solution. Evaporated to dryness, and treated with cold ether, it yields
      - An olive-coloured acid substance, soluble in ether and in hot alcohol, but not precipitated in the cold solution. Found by the addition of milk of lime, with the application of heat, to consist of two substances, viz.
        - A first substance precipitated by the lime, which decomposed with sulphuric acid, yields to hot ether the pure immediate principle, *Excretoleic acid*.
        - A second substance, dissolved in the hot filtrate from the above lime precipitate, being *Excretine*, or a body closely allied to it.
      - A yellow substance insoluble in ether, and partly soluble in water.
  - Substance soluble in hot alcoholic extract remaining dissolved in the fluid when cold. This solution is treated with milk of lime.
    - Precipitate obtained by the addition of milk of lime to the alcoholic solution.
      - The precipitate treated with ether, and the ethereal solution evaporated spontaneously, yields
        - *Excretine*.
        - A yellow oily matter, hitherto undescribed.
      - Precipitate, free from excretine, dissolved in alcohol or decomposed in water by hydrochloric acid, yields
        - *Margaric acid* (not constantly present).
        - *Colouring matter* of excrements.
    - Filtrate from lime precipitate concentrated to a semifluid consistence.
      - Treated with ether, often yields excretine.
      - Concentrated filtrate, free from excretine, decomposed with sulphuric acid and distilled, does not yield any butyric acid.

XII. *On the Effect of the Pressure of the Atmosphere on the Mean Level of the Ocean.*

By Captain Sir James Clark Ross, *R.N., D.C.L., F.R.S. &c.*

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In September 1848 Her Majesty's ships Enterprize and Investigator entered the harbour of Port Leopold, in latitude 74° N. and longitude 91° W., for the purpose of establishing there a depôt of provisions, and of extending, in boats, the examination of the north, south, and west coasts of North Somerset, in search of the missing expedition under the command of Sir John Franklin. No sooner, however, were the ships anchored, than a heavy pack of ice was driven down upon, and completely closed the harbour's mouth, and this effectually preventing their egress, they were compelled there to pass the winter of 1848–49.

It was during that period that the series of observations, which I have now the honour of submitting to the consideration of the Royal Society, on the effect of the pressure of the atmosphere on the level of the ocean, was obtained, and as it was made under peculiarly favourable circumstances, which I shall presently point out, I have no doubt it will contribute to throw some light on the movements of the tides, and on some of the causes of their apparent irregularities, not only in the Polar regions, but also along our own coasts, which have not hitherto been detected, or have not received that attention their importance demands.

It originated in the following circumstances:—Soon after the harbour had been completely frozen over, a very heavy pressure from the main pack forced the newly-formed sheet of ice, which covered the bay, far up towards its head, carrying the ships with it into such shallow water that at low spring-tides their keels sometimes rested on the ground.

It is well known that from many causes great differences in the rise or fall of the tides occur in nearly all latitudes, and as any extraordinary depression, in our case, might seriously injure the ships with so great a weight of ice attached to their sides, the movements of the tides necessarily became to me an object of great anxiety and of careful observation, in order, if possible, to ascertain the amount of irregularities to which they were liable in this particular locality, and to investigate the cause.

The first few days' observations evidenced much larger differences in the elevation or depression of successive high or low waters than could be accounted for by any of the generally received causes of disturbance; and I was at once led to connect them with the changes of pressure of the atmosphere, from perceiving that high water was not so high, and that low water was lower, on the days that the pressure of the atmosphere was greater, and that high water was too high, and low water not so low as it ought to have been, on the days of smaller atmospheric pressure.

The observations during September and October were limited to the register of

high and low water, but various causes of disturbance so frequently masked the effects of the pressure of the atmosphere, that the four observations on each day were not sufficient to determine the amount of effect of its variations: and also, owing to the semidiurnal inequality and other causes of derangement, the usual mode of determining the level, by taking the mean between successive high and low waters, was found inadequate to the detection of small quantities arising from variation of pressure. I therefore adopted a different system of observation from any that has heretofore been practised, in order to determine the mean level of the ocean on each day.

I began by instituting simultaneous observations of the height of the tide and of the mercury in the barometer at every quarter of an hour throughout the day and night, and from these I found that the mean level of the ocean for each day could be determined with a great degree of accuracy, and that the variation in the daily mean level and in the mean pressure of the atmosphere, as indicated by the barometer, followed each other in a very remarkable manner, but in an inverse ratio, which could only be accurately obtained by a much more extended series of observations.

But the fatigue of making a long-continued series of observations of this nature, at every quarter of an hour, during the inclemency of an arctic winter, was greater than I could expect the officers to endure who had thenceforward to continue the observations which I had begun. Hourly observations were at length determined on. Those which I had previously made having been several times interrupted by the necessity of moving the ships into deeper water, could not be brought into strict comparison with each other without such a complication of corrections to be applied to each set as would have greatly and uselessly extended this communication; they have, therefore, not been employed, and the conclusions which have been arrived at are entirely derived from the observations contained in the following tables.

The peculiar advantages of our position at Port Leopold, to which I have before alluded, for making tidal observations were,—

1st. In the great width of the entrance of the harbour admitting the free ingress and egress of the waters, combined with the large field of ice which covered the whole extent of the bay, containing more than ten square miles of surface, and completely subduing those undulations of the water, which in other places render tidal observations uncertain.

2nd. In the steady movement of this immense platform of ice, rising and falling with such singular regularity and precision as to admit the reading off the marks of the tide-pole with the greatest exactness, even to the tenth of an inch; although such minuteness was not always attempted, the nearest quarter of an inch being generally deemed sufficient.

3rd. The shallowness of the water, and the evenness and solidity of the clay bottom admitting the fixture of the tide-pole with immoveable firmness.

4th. The whole surface of the ocean in the neighbourhood being, for the greater part of the time, covered by a sheet of ice, preventing those irregularities which occur in other localities from the violence of the wind raising or depressing the ocean in as many different degrees as it varies either in strength or direction.

The ships were not finally placed in their winter position until the middle of October, when the operation of fixing the tide-pole engaged our first attention.

A hole, 2 feet square, was cut through the icy platform, a strong pole, nearly 40 feet long, passed through it, and driven firmly down several feet into the clay, and fixed by heavy iron weights, which also rested on the clay and prevented any movement of the pole. It was placed in about 21 feet depth of water at the time of mean level of the sea, and by the end of the month was considered, and afterwards proved to have been so perfectly immoveable, that we began the regular series of observations on the 1st of November.

Another tide-pole was in like manner fixed through a hole in the ice close to the Investigator, for the sake of reference and comparison. Hourly observations of the tide and the barometer were made by the officers and petty officers of that ship, exactly corresponding with those made by the officers of the Enterprize, throughout the whole of the nine following months, to the end of July, and they proved of great value in many instances, where very large and apparently unaccountable irregularities of the tides occurred, and which otherwise might have been attributed to inaccuracy of observation, or of registry, or of the shifting of the tide-pole, had they not also been observed in every case, at exactly the same time and precisely to the same amount at both the tide-poles.

The reduction of the double series of observations, however, would have so greatly increased the labour of preparing this paper as well as its length, that the Investigator's observations have, for the present, been only used for comparison in several cases of uncertainty above alluded to, and for the purpose of refixing the tide-pole of the Enterprize when it was lifted by the ice on the 18th of December. But the whole of the observations of both the ships are preserved in the proper office at the Admiralty, and may at any time be referred to for any purposes of further investigation.

The hourly observations which were commenced on the 1st of November, were continued uninterruptedly until the morning of the 18th of December, when the tide-pole having been frozen to the underpart of the ice was drawn out of the ground as the tide rose, and thus made the first break in the series, after forty-seven complete days. The amount of displacement of the pole was easily determined by comparison with that of the Investigator, but several days elapsed before it could be satisfactorily fixed at the same point in which it originally stood.

Subsequent observations serve to show that from this time to the middle of July there was a progressive elevation of the mean level of the ocean, and, although of small amount, the difference from month to month was sufficiently evident to render subdivisions of the series desirable, in order that the individual observations of each separate division should be strictly comparable with the others; so that this early interruption is the less to be regretted.

The method of observation was as follows:—At the exact hour of mean time the heights of the tide and of the mercury in the barometer were taken; the former by the quarter-master, and the latter by the officer of the watch, who immediately entered both the observations in the meteorological journal, from which the following tables were constructed.

TABLE I.—Showing the height of the sea, and the corresponding height of the mercury in the barometer, for every hour, during the month of November 1848, at Port Leopold.

Hour.	November 1.		November 2.		November 3.		November 4.		November 5.		November 6.	
	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.
A.M.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.
1	21 11·5	30·122	21 3·0	30·034	21 7·0	29·355	20 8·0	29·379	19 6·5	29·980	19 4·0	30·286
2	22 2·0	30·122	21 9·0	30·017	22 1·0	29·356	21 1·0	29·388	19 10·0	30·004	19 1·0	30·294
3	21 8·5	30·127	21 10·0	30·000	22 5·0	29·350	21 6·0	29·397	20 2·0	30·026	19 4·0	30·299
4	21 3·5	30·132	21 6·0	29·978	22 4·0	29·352	21 8·0	29·404	20 6·0	30·045	19 9·0	30·300
5	20 1·5	30·139	20 10·0	29·951	22 0·0	29·318	21 8·0	29·432	20 9·0	30·054	20 2·0	30·308
6	19 2·0	30·147	19 11·0	29·926	21 6·0	29·320	21 6·0	29·460	20 11·0	30·070	20 9·0	30·301
7	18 5·5	30·142	19 2·0	29·897	20 11·0	29·324	21 1·5	29·505	20 10·5	30·097	21 0·5	30·295
8	18 2·0	30·129	18 11·0	29·868	20 4·5	29·342	20 8·5	29·520	20 7·0	30·102	21 1·5	30·296
9	18 5·5	30·103	18 11·5	29·833	20 1·0	29·354	20 4·0	29·548	20 2·5	30·118	20 10·0	30·285
10	19 2·2	30·100	19 6·0	29·779	20 2·5	29·364	20 1·0	29·574	19 10·5	30·154	20 7·0	30·272
11	20 4·0	30·113	20 5·0	29·746	20 6·0	29·362	20 0·5	29 603	19 8·0	30·166	20 1·5	30·265
Noon	21 6·0	30·108	21 6·0	29·683	21 1·5	29·362	20 4·5	29·637	19 8·0	30·186	19 8·0	30·265
1	22 11·0	30·110	22 7·0	29·655	22 0·5	29·354	21 0·0	29·658	20 1·0	30·207	19 6·0	30·272
2	23 6·5	30·104	23 5·0	29·619	22 10·0	29·356	21 9·0	29·689	20 8·0	30·213	19 7·0	30·272
3	23 8·5	30·102	23 11·0	29·609	23 5·0	29 348	22 2·0	29·713	21 1·0	30·225	20 0·0	30·270
4	23 4·0	30·092	23 11·0	29·547	23 9·0	29·355	22 11·0	29·723	21 11·0	30·229	20 8·0	30·260
5	22 6·0	30·085	23 7·0	29·503	23 7·5	29·353	23 1·0	29·751	22 5·0	30·241	21 5·0	30·258
6	21 6·0	30·090	22 11·0	29·452	23 2·0	29·351	22 10·0	29·799	22 9·0	30·265	22 3·5	30·267
7	20 6·5	30·080	22 1·0	29·437	22 6·0	29·349	22 7·0	29·819	22 9·0	30·263	22 7·5	30·260
8	19 8·5	30·074	21 4·0	29·412	21 7·0	29·350	22 2·0	29·836	22 4·5	30·271	22 9·0	30·254
9	19 5·0	30·067	20 10·5	29·385	21 3·0	29·351	21 6·0	29·863	21 9·0	30·281	22 6·0	30 238
10	19 7·0	30·056	20 8·0	29·375	20 7·0	29·364	20 8·0	29·883	21 0·0	30·273	21 11·0	30·234
11	19 11·5	30·046	20 10·5	29·346	20 4·0	29·369	20 0·0	29·906	20 3·0	30·273	21 0·0	30·228
Midnight	20 8·0	30·034	21 2·0	29·356	20 5·0	29·374	19 7·5	29·953	19 8·5	30·278	20 2·5	30·214
Mean ...	20 9·9	30·101	21 4·4	29·683	21 8·3	29·351	21 3·5	29·643	20 9·7	30·168	20 8·1	30·270

Hour.	November 7.		November 8.		November 9.		November 10.		November 11.		November 12.	
	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.
A.M.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.
1	19 5·0	30·212	19 9·5	29·934	20 6·0	29·656	21 6·5	29·761	22 6·5	29·823	23 5·0	29 892
2	18 11·5	30·215	18 11·0	29·902	19 4·0	29·667	20 1·0	29·769	21 1·0	29·827	21 11·0	29·901
3	18 10·5	30·215	18 6·5	29·882	18 5·0	29·675	18 10·0	29·771	19 4·5	29·855	20 5·5	29·903
4	19 2·0	30·206	18 7·0	29·843	18 1·0	29·680	17 10·0	29·774	18 1·0	29 865	18 10·5	29·916
5	19 7·5	30·185	18 11·0	29·840	18 5·0	29·681	17 8·2	29·756	17 4·0	29·877	17 6·0	29·913
6	20 8·5	30·182	20 2·0	29·809	19 1·5	29·683	18 6·0	29·754	17 6·0	29·886	17 2·5	29·921
7	21 3·5	30·177	21 4·0	29·782	19 5·5	29·686	19 5·5	29·758	18 8·0	29·898	17 7·5	29·925
8	21 9·0	30·167	22 2·0	29·770	21 9·5	29·683	21 0·0	29·775	20 1·0	29·902	18 10·0	29·939
9	21 10·5	30·162	22 10·5	29·745	23 2·0	29·675	22 10·0	29·752	22 0·5	29·899	20 10·0	29·962
10	21 7·5	30·161	22 11·5	29·723	23 8·5	29·683	23 10·5	29·742	23 7·0	29·907	22 0·0	29·976
11	21 1·5	30·159	22 7·5	29·718	23 9·0	29·694	24 0·0	29·733	23 8·0	29·915	24 5·0	29·995
Noon	20 6·0	30·136	22 1·0	29·718	23 1·5	29·694	23 10·5	29·730	23 9·0	29·915	25 4·0	30·023
1	19 9·5	30·114	20 11·0	29·711	22 0·5	29·707	23 0·0	29·728	23 8·5	29·919	25 4·0	30·047
2	19 4·5	30·132	19 11·7	29·721	20 10·0	29·723	21 9·0	29·739	22 10·0	29·919	24 6·0	30·093
3	19 5·5	30·112	19 4·5	29·719	19 9·0	29·703	20 3·0	29·745	21 3·5	29·921	22 11·5	30·122
4	19 9·0	30·114	19 4·0	29·721	19 2·5	29·745	19 5·0	29·746	19 8·0	29·916	21 5·5	30·141
5	20 6·0	30·094	19 7·5	29·727	19 3·5	29·730	18 10·0	29·749	18 6·0	29·923	19 8·0	30·172
6	21 3·5	30·076	20 9·0	29·740	19 6·0	29·746	18 10·0	29·749	18 1·0	29·916	18 6·0	30·192
7	22 1·0	30·087	21 8·0	29·725	20 3·5	29·744	19 9·5	29·756	18 6·0	29·914	18 3·5	30·193
8	22 8·5	30·057	22 7·0	29 717	21 10·0	29·735	21 0·0	29 773	19 2·0	29 912	18 8·0	30·215
9	22 10·5	30 010	23 3·0	29·693	23 1·0	29·729	22 2·0	29·786	21 0·0	29·906	19 7·0	30·227
10	22 11·5	30·001	23 6·5	29·671	23 8·0	29·734	23 4·0	29·788	22 4·5	29 896	20 11·0	30·241
11	21 11·0	29·986	22 11·5	29·665	23 7·5	29·744	23 10·0	29·796	23 5·0	29·877	22 3·0	30·248
Midnight	20 10·5	29 963	22 0·0	29·661	22 9·0	29·750	23 8·5	29 806	23 9·5	29·877	22 11·5	30·271
Mean ...	20 9·2	30·123	21 0·4	29·756	21 0·4	29·706	21 0·7	29·759	20 10·0	29·894	20 11·7	30 064

TABLE I.—November 1848. (Continued.)

Hour.	November 13.		November 14.		November 15.		November 16.		November 17.		November 18.	
	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.
A.M.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.
1	22 10·0	30·277	23 2·0	30·090	22 5·5	30·058	21 2·0	30·105	20 3·0	29·840	20 0·0	29·697
2	22 1·0	30·287	23 2·0	30·079	22 11·0	30·076	21 11·5	30·098	21 1·0	29·817	20 5·0	29·699
3	20 10·0	30·290	22 4·0	30·058	22 8·5	30·081	22 3·2	30·081	21 7·0	29·813	20 9·5	29·704
4	19 7·0	30·298	20 11·0	30·063	21 10·0	30·095	22 0·0	30·069	21 9·5	29·795	21 5·0	29·714
5	17 7·0	30·297	19 5·0	30·049	20 7·0	30·135	21 4·0	30·062	21 8·5	29·765	21 8·0	29·719
6	16 8·0	30·299	18 4·0	30·030	19 3·5	30·155	20 3·0	30·043	21 1·5	29·749	21 9·0	29·719
7	16 6·0	30·299	17 3·0	30·024	18 3·0	30·188	19 2·0	30·026	20 7·0	29·742	21 6·5	29·725
8	17 1·5	30·294	17 4·0	30·017	17 7·5	30·208	18 6·0	29·997	19 5·0	29·741	20 11·0	29·727
9	18 8·5	30·292	18 2·0	30·025	17 11·0	30·226	18 3·0	29·985	19 1·0	29·727	20 3·5	29·753
10	20 6·0	30·289	19 7·5	30·029	19 1·0	30·245	18 8·5	29·971	19 0·0	29·705	19 8·0	29·759
11	22 4·5	30·279	21 6·0	30·035	20 9·0	30·250	19 7·5	29·956	19 3·5	29·713	19 6·5	29·779
Noon	24 0·5	30·277	23 3·0	30·028	21 5·0	30·246	20 11·0	29·942	19 11·5	29·701	19 8·0	29·789
1	24 9·2	30·239	24 8·0	30·039	23 6·0	30·254	22 5·5	29·935	21 3·5	29·705	20 3·5	29·802
2	24 9·0	30·221	25 0·5	30·052	24 6·0	30·260	23 9·0	29·931	22 3·5	29·705	20 10·5	29·808
3	23 9·0	30·188	24 8·0	30·056	24 8·5	30·258	24 3·5	29·906	23 2·5	29·705	21 9·5	29·804
4	22 3·0	30·185	23 8·0	30·058	24 4·0	30·258	24 6·0	29·902	23 11·0	29·691	22 7·0	29·814
5	20 8·0	30·194	22 2·5	30·060	23 0·0	30·244	24 0·0	29·904	23 11·0	29·686	23 1·0	29·832
6	19 0·0	30·168	20 6·5	30·063	21 3·0	30·223	23 0·5	29·902	23 6·0	29·686	23 2·5	29·827
7	18 3·0	30·149	19 2·0	30·056	20 1·0	30·195	21 6·5	29·890	22 10·0	29·686	22 11·5	29·835
8	18 2·0	30·142	18 7·0	30·048	19 1·0	30·191	20 7·0	29·869	21 11·0	29·684	22 5·0	29·850
9	18 9·5	30·122	18 6·0	30·038	18 6·0	30·175	19 7·0	29·848	21 0·5	29·695	21 9·0	29·845
10	19 11·0	30·115	19 1·0	30·040	18 6·0	30·146	19 1·5	29·844	20 1·5	29·696	20 9·5	29·845
11	21 4·0	30·101	20 3·0	30·043	19 0·0	30·146	19 3·0	29·833	19 8·0	29·696	19 11·0	29·844
Midnight	22 3·5	30·091	21 6·0	30·045	20 1·0	30·123	19 7·5	29·838	19 7·0	29·696	19 4·0	29·848
Mean ...	20 6·4	30·225	20 11·2	30·047	20 10·7	30·185	21 1·0	29·957	21 2·1	29·727	21 1·2	29·780

Hour.	November 19.		November 20.		November 21.		November 22.		November 23.		November 24.	
	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.
A.M.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.
1	19 1·0	29·858	19 4·5	29·672	19 8·0	29·771	19 10·0	29·924	20 6·0	29·961	21 9·5	29·901
2	19 4·0	29·850	19 2·5	29·677	18 11·0	29·790	18 11·0	29·929	19 7·0	29·949	20 1·0	29·903
3	19 10·0	29·847	19 5·5	29·671	18 9·5	29·797	18 6·0	29·931	18 7·0	29·954	19 0·5	29·908
4	20 6·0	29·830	19 10·0	29·651	19 0·5	29·799	18 5·0	29·937	18 3·0	29·957	18 6·0	29·909
5	21 1·0	29·822	20 6·0	29·652	19 8·0	29·799	18 11·0	29·934	18 7·0	29·962	18 0·5	29·919
6	21 5·5	29·819	21 2·0	29·656	20 6·0	29·804	19 9·0	29·929	19 8·0	29·955	18 9·5	29·910
7	21 6·0	29·800	21 10·0	29·662	21 4·5	29·808	20 9·0	29·932	20 6·0	29·957	19 9·0	29·900
8	21 5·0	29·798	22 2·0	29·672	22 0·0	29·815	21 10·5	29·924	21 8·0	29·957	20 11·0	29·898
9	21 1·0	29·774	22 0·0	29·687	22 5·0	29·811	22 7·0	29·929	22 9·5	29·957	22 5·0	29·889
10	20 7·5	29·760	21 8·0	29·696	22 3·0	29·816	22 10·0	29·937	23 5·0	29·960	23 5·5	29·879
11	20 2·0	29·757	21 1·0	29·696	21 10·0	29·822	22 7·0	29·937	23 6·0	29·952	23 11·5	29·870
Noon	19 11·2	29·738	20 3·0	29·712	21 1·5	29·831	22 0·5	29·929	23 1·0	29·934	23 9·2	29·880
1	19 11·5	29·748	20 0·5	29·712	20 5·5	29·853	21 1·5	29·935	22 2·0	29·930	22 6·0	29·891
2	20 3·0	29·766	19 11·0	29·712	19 8·5	29·861	20 2·5	29·937	21 2·0	29·922	21 11·5	29·897
3	20 11·0	29·751	20 1·0	29·717	19 6·5	29·875	19 6·5	29·953	20 1·0	29·927	20 7·0	29·896
4	21 7·0	29·700	20 7·0	29·717	19 9·0	29·881	19 4·0	29·951	19 5·5	29·922	20 3·0	29·880
5	22 3·5	29·701	21 3·0	29·717	20 2·0	29·888	19 6·5	29·943	19 3·0	29·919	19 3·0	29·897
6	22 9·0	29·699	21 11·5	29·725	21 0·0	29·899	20 2·0	29·943	19 8·0	29·936	19 2·5	29·888
7	23 0·5	29·700	22 8·0	29·723	21 9·0	29·903	21 1·0	29·945	20 6·0	29·930	19 9·0	29·898
8	22 10·0	29·682	22 11·0	29·730	22 2·5	29·903	21 10·5	29·948	21 4·0	29·930	20 9·0	29·897
9	22 5·0	29·664	22 7·5	29·740	22 6·0	29·896	22 3·5	30·034	22 1·0	29·922	21 9·0	29·894
10	21 8·5	29·664	22 4·0	29·737	22 3·5	29·896	22 7·0	30·084	22 8·0	29·908	22 7·0	29·892
11	20 8·0	29·669	21 6·5	29·751	21 9·0	29·898	22 3·5	30·128	22 9·0	29·902	22 10·5	29·901
Midnight	20 0·0	29·669	20 7·5	29·777	20 11·0	29·913	21 7·0	30·006	22 2·0	29·898	22 10·0	29·908
Mean ...	21 0·2	29·753	21 0·5	29·703	20 9·8	29·847	21 2·3	29·953	20 11·2	29·937	21 0·2	29·896

Table I.—November 1848. (Continued.)

Hour.	November 25.		November 26.		November 27.		November 28.		November 29.		November 30.	
	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.
A.M.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.
1	21 9·5	29·908	22 1·0	29·930	22 6·0	29·861	22 4·5	29·822	22 4·0	29·701	22 1·0	29·840
2	20 8·0	29·914	21 2·0	29·940	21 8·0	29·853	21 11·0	29·821	22 3·5	29·706	22 2·5	29·854
3	19 7·0	29·889	20 1·0	29·946	20 6·0	29·849	20 11·0	29·799	21 6·5	29·708	21 10·0	29·854
4	18 7·0	29·891	19 0·0	29·944	19 5·0	29·847	19 11·0	29·791	20 9·0	29·712	21 2·5	29·856
5	18 2·0	29·886	18 3·0	30·025	18 5·0	29·858	18 8·0	29·819	19 7·5	29·717	20 1·5	29·863
6	18 1·5	29·868	18 1·0	30·052	18 1·0	29·847	18 2·0	29·821	18 9·0	29·719	19 1·0	29·866
7	19 1·0	29·872	18 8·0	30·033	18 3·0	29·836	17 11·5	29·821	18 3·0	29·693	18 7·0	29·862
8	20 3·5	29·874	20 5·0	30·006	19 1·0	29·830	18 5·5	29·821	18 5·0	29·691	18 4·5	29·869
9	21 4·5	29·875	21 3·5	29·939	20 7·0	29·827	19 9·0	29·823	19 4·5	29·681	18 11·5	29·874
10	23 3·0	29·862	22 1·0	29·933	22 1·5	29·823	21 4·0	29·814	20 8·0	29·685	20 1·0	29·887
11	24 2·0	29·858	24 0·5	29·931	23 3·5	29·822	22 7·0	29·789	21 10·5	29·684	21 3·0	29·901
Noon	24 4·5	29·878	24 7·0	29·919	24 3·0	29·785	23 9·0	29·775	23 5·0	29·708	22 6·0	29·910
1	23 10·0	29·865	24 5·0	29·917	24 5·0	29·785	24 4·5	29·763	24 4·0	29·730	23 9·0	29·913
2	22 10·0	29·867	23 9·0	29·921	23 11·0	29·809	24 4·0	29·754	24 6·5	29·730	24 2·5	29·906
3	21 7·5	29·871	22 6·5	29·924	23 0·0	29·808	23 5·0	29·755	24 1·5	29·723	24 2·5	29·912
4	20 4·0	29·873	21 2·5	29·917	22 4·0	29·803	22 5·5	29·745	23 3·0	29·728	23 7·0	29·920
5	19 5·0	29·883	20 1·5	29·912	20 6·0	29·821	21 5·0	29·757	22 3·0	29·752	22 6·0	29·928
6	19 1·0	29·894	19 3·5	29·915	19 5·0	29·826	20 3·0	29·753	20 10·5	29·764	21 7·0	29·937
7	19 4·0	29·904	19 2·0	29·915	19 0·0	29·831	19 5·0	29·745	19 11·0	29·764	20 5·5	29·941
8	20 0·5	29·906	19 8·0	29·907	19 0·2	29·840	19 2·5	29·738	19 2·0	29·778	19 7·5	29·945
9	20 11·5	29·912	20 5·0	29·904	19 9·0	29·847	19 6·0	29·719	19 2·0	29·801	19 5·0	29·947
10	21 10·5	29·926	21 6·0	29·892	20 8·0	29·836	20 2·5	29·710	19 10·0	29·803	19 6·0	29·957
11	22 6·5	29·928	22 3·0	29·897	21 9·0	29·837	21 1·0	29·705	20 8·0	29·815	20 1·5	29·957
Midnight	22 7·5	29·928	22 6·5	29·850	23 1·0	29·837	22 0·0	29·698	21 6·0	29·821	20 10·5	29·962
Mean ...	21 0·0	29·889	21 1·3	29·936	21 0·5	29·830	20 11·6	29·773	21 1·5	29·753	21 1·1	29·903

December 1848.

Hour.	December 1.		December 2.		December 3.		December 4.		December 5.		December 6.	
	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.
A.M.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.
1	21 7·0	29·959	20 11·5	29·919	20 3·5	29·983	19 10·0	29·886	19 0·5	29·815	18 10·0	29·835
2	21 11·2	29·966	21 7·0	29·930	21 0·0	29·971	20 3·5	29·859	19 4·5	29·811	18 7·5	29·860
3	21 11·0	29·978	21 11·0	29·932	21 6·0	29·967	20 11·0	29·864	19 10·5	29·810	18 10·0	29·877
4	21 6·0	29·980	21 9·0	29·938	21 10·0	29·946	21 6·0	29·865	20 6·0	29·803	19 6·0	29·896
5	20 9·0	29·997	21 2·0	29·934	21 9·0	29·938	21 8·0	29·867	21 0·0	29·808	20 3·0	29·939
6	19 11·0	30·002	20 7·5	29·947	21 4·5	29·935	21 10·0	29·869	21 5·5	29·797	21 1·0	29·943
7	19 1·0	30·000	19 10·0	29·961	20 9·5	29·931	21 8·5	29·876	21 7·0	29·799	21 9·0	29·964
8	18 8·0	30·162	19 2·0	29·975	20 2·5	29·935	20 10·5	29·864	21 6·0	29·784	22 0·5	29·962
9	18 10·0	29·971	19 0·0	29·979	19 7·0	29·933	20 5·0	29·861	21 1·5	29·784	21 10·0	29·967
10	19 6·0	29·958	19 2·5	29·989	19 4·0	29·934	20 0·5	29·859	20 8·0	29·780	21 6·0	29·976
11	20 6·5	29·957	19 10·5	30·002	19 6·0	29·954	19 10·5	29·846	20 3·0	29·772	20 9·0	29·995
Noon	21 8·0	29·952	20 10·0	30·018	20 1·5	29·947	20 0·0	29·836	19 11·0	29·776	20 0·5	30·007
1	22 10·5	29·953	21 11·5	30·041	21 0·5	29·950	20 6·0	29·826	19 9·5	29·750	19 6·0	30·021
2	23 9·0	29·953	22 10·0	30·041	22 0·5	29·950	21 3·0	29·830	20 0·5	29·758	19 3·5	30·039
3	24 1·5	29·950	23 6·5	30·049	22 9·5	29·949	22 0·0	29·822	20 9·0	29·773	19 8·0	30·045
4	23 10·5	29·945	23 8·0	30·051	23 4·0	29·949	22 5·5	29·837	21 3·5	29·778	20 2·5	30·055
5	23 2·5	29·937	23 5·5	30·057	23 4·0	29·950	22 11·5	29·824	22 2·0	29·788	20 10·5	30·061
6	22 5·5	29·914	22 9·0	30·053	23 1·0	29·939	23 2·0	29·824	22 8·0	29·789	21 8·5	30·079
7	21 2·5	29·912	21 11·0	30·048	22 11·0	29·929	22 9·0	29·824	22 10·5	29·793	22 6·0	30·078
8	20 6·5	29·907	21 0·0	30·053	21 7·0	29·931	22 3·0	29·824	22 7·5	29·811	22 8·5	30·084
9	19 9·0	29·902	20 2·0	30·068	20 9·0	29·911	21 5·0	29·826	22 0·0	29·799	22 5·0	30·097
10	19 8·0	29·910	19 9·0	30·044	19 11·0	29·891	20 5·0	29·822	21 2·5	29·801	21 9·0	30·096
11	20 0·5	29·902	19 8·0	29·995	19 6·0	29·898	19 8·5	29·822	20 2·5	29·818	20 10·0	30·094
Midnight	20 5·0	29·904	19 10·0	30·010	19 5·0	29·891	19 3·0	29·813	19 3·5	29·822	19 9·0	30·111
Mean ...	21 1·9	29·957	21 1·2	30·002	21 1·5	29·938	21 1·3	29·843	20 10·6	29·792	20 8·1	30·001

Table I.—December 1848. (Continued.)

Hour.	December 7.		December 8.		December 9.		December 10.		December 11.		December 12.	
	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.
A.M.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.
1	18 9·0	30·122	19 4·0	30·054	20 10·0	29·738	21 9·0	29·828	22 6·0	29·909	23 1·5	29·870
2	18 2·0	30·142	18 0·0	30·061	19 6·0	29·743	20 4·0	29·849	21 2·0	29·910	22 4·0	29·883
3	18 1·0	30·141	17 11·0	30·056	18 4·5	29·745	18 9·0	29·854	19 8·0	29·914	21 0·0	29·891
4	18 6·0	30·151	17 11·0	30·043	17 9·5	29·751	17 9·0	29·856	18 5·0	29·896	19 6·0	29·901
5	19 4·0	30·146	18 8·0	30·035	17 11·0	29·753	17 3·5	29·873	17 3·5	29·917	18 2·0	29·888
6	20 4·0	30·145	19 7·5	30·032	18 8·5	29·755	17 7·0	29·887	16 11·5	29·912	17 2·0	29·888
7	21 5·0	30·147	21 0·5	30·010	20 2·0	29·758	18 3·0	29·891	17 8·0	29·914	17 1·5	29·893
8	22 3·0	30·139	22 5·5	29·987	21 10·0	29·755	20 5·5	29·895	19 1·0	29·901	18 0·0	29·896
9	22 9·0	30·132	23 2·5	29·966	23 6·0	29·750	22 3·0	29·900	20 10·5	29·867	19 9·5	29·888
10	22 6·0	30·132	23 11·0	29·953	24 4·0	29·754	23 11·0	29·914	23 0·5	29·866	21 9·5	29·785
11	21 11·0	30·130	23 8·5	29·921	24 9·0	29·751	24 10·0	29·912	24 4·0	29·865	23 8·0	29·787
Noon	21 0·0	30·123	22 6·5	29·911	24 3·0	29·745	24 11·5	29·914	25 4·0	29·862	25 0·0	29·889
1	20 2·0	30·124	21 10·0	29·899	23 11·0	29·755	24 3·0	29·917	25 3·0	29·858	25 3·5	29·886
2	19 5·0	30·117	20 7·5	29·881	21 10·0	29·768	23 0·0	29·924	24 2·0	29·862	25 0·5	29·895
3	19 2·0	30·115	19 10·0	29·856	20 6·0	29·755	21 4·0	29·928	22 10·5	29·860	24 2·0	29·894
4	19 5·0	30·115	19 5·0	29·849	19 6·0	29·769	20 2·0	29·924	21 1·0	29·869	22 7·5	29·898
5	20 0·0	30·111	19 5·0	29·820	19 1·0	29·781	18 11·0	29·927	19 6·0	29·862	20 10·0	29·903
6	20 10·0	30·109	20 1·0	29·814	19 3·0	29·780	18 4·0	29·938	18 7·0	29·867	19 4·0	29·901
7	21 8·5	30·108	20 11·0	29·803	19 10·0	29·782	18 8·0	29·940	18 5·0	29·862	18 5·0	29·906
8	22 3·5	30·106	22 1·0	29·792	20 10·5	29·793	19 7·0	29·966	18 10·5	29·862	18 4·0	29·909
9	22 8·0	30·099	22 10·0	29·746	22 2·5	29·795	20 10·0	29·926	19 11·0	29·869	18 7·0	29·908
10	22 6·0	30·095	23 4·0	29·728	23 0·0	29·793	22 0·5	29·924	21 4·0	29·874	20 1·0	29·900
11	21 8·0	30·085	23 0·0	29·728	23 3·5	29·805	22 11·5	29·929	22 5·0	29·867	21 3·0	29·910
Midnight	20 7·0	30·079	22 2·0	29·733	22 10·0	29·822	23 0·0	29·908	23 1·5	29·868	22 8·0	29·930
Mean ...	20 7·7	30·121	20 11·9	29·903	21 2·0	29·766	20 10·6	29·905	20 11·0	29·879	20 11·6	29·887

Hour.	December 13.		December 14.		December 15.		December 16.		December 17.		December 18.
	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	Tide.	Barom.	
A.M.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	ft. in.	inches.	
1	22 11·0	29·914	22 7·0	29·847	21 10·5	29·736	20 9·0	29·762	19 10·0	29·936	Tide-pole frozen into the ice, and lifted with the rising tide above 4 inches.
2	22 10·0	29·910	23 0·5	29·833	22 7·0	29·726	21 8·5	29·769	20 8·0	29·942	
3	21 11·0	29·915	22 9·5	29·825	22 9·5	29·718	22 3·0	29·776	21 5·0	29·953	
4	20 7·5	29·911	21 10·0	29·823	22 6·5	29·721	22 5·0	29·778	21 11·0	29·965	
5	19 0·0	29·926	20 6·5	29·805	21 7·5	29·717	22 1·0	29·788	21 10·0	29·961	
6	17 11·0	29·925	19 4·5	29·808	20 7·0	29·715	21 4·0	29·802	21 6·0	29·968	
7	17 8·0	29·911	18 3·0	29·808	19 6·0	29·710	20 6·0	29·797	21 1·0	29·982	
8	17 5·0	29·899	17 11·0	29·808	18 10·0	29·711	19 5·0	29·808	20 6·0	29·995	
9	18 6·0	29·894	18 5·0	29·793	18 9·0	29·705	19 2·5	29·805	19 11·5	30·010	
10	20 3·0	29·878	19 4·0	29·783	19 1·0	29·710	19 0·0	29·803	19 6·0	30·028	
11	22 2·0	29·875	21 1·0	29·776	20 1·0	29·710	19 6·0	29·812	19 5·5	30·043	
Noon	23 10·5	29·875	22 9·0	29·774	21 3·0	29·707	20 5·5	29·827	19 8·0	30·050	
1	25 1·0	29·886	24 3·0	29·792	22 11·0	29·697	21 6·0	29·845	20 1·0	30·075	
2	25 5·0	29·895	25 1·0	29·823	24 1·0	29·705	22 9·0	29·848	21 2·0	30·094	
3	25 0·0	29·878	25 1·0	29·802	24 10·0	29·700	23 8·5	29·849	22 1·2	30·106	
4	23 11·0	29·872	24 8·0	29·800	24 8·0	29·692	24 0·5	29·858	22 8·5	30·101	
5	22 3·5	29·890	23 7·0	29·784	24 2·0	29·711	23 11·0	29·859	23 1·0	30·111	
6	20 11·0	29·889	22 6·0	29·771	23 0·5	29·719	23 2·5	29·873	22 10·5	30·120	
7	20 3·0	29·885	20 7·0	29·769	21 8·0	29·731	22 3·0	29·883	22 1·0	30·120	
8	18 6·0	29·879	19 5·5	29·758	20 3·0	29·727	21 2·5	29·883	21 7·0	30·128	
9	18 7·0	29·863	18 9·0	29·761	19 5·5	29·742	20 0·0	29·902	20 7·0	30·136	
10	19 1·0	29·853	18 11·0	29·743	19 2·0	29·740	19 4·0	29·908	19 8·0	30·148	
11	20 4·5	29·847	19 8·0	29·739	19 5·0	29·740	19 0·0	29·922	19 2·0	30·140	
Midnight	21 8·0	29·837	20 9·0	29·736	19 11·0	29·742	19 3·5	29·930	18 11·0	30·144	
Mean ...	21 1·0	29·887	21 3·6	29·790	21 4·5	29·718	21 2·4	29·837	20 10·7	30·052	

Explanation of Tables A. and B. which follow:—

From the preceding Tables, the arithmetic mean of the hourly observations of the height of the sea for each day is taken as the mean level of the ocean for that day, and the mean of the hourly observed heights of the barometer as the corresponding mean pressure of the atmosphere; these mean levels, and corresponding mean pressures, are brought together in the following Table A., arranged in the order of the days of observation.

In Table B., commencing with the day of greatest mean pressure, they are arranged in the order of the mean heights of the barometer, with the corresponding mean levels, without regard to the dates of observation, for the purpose of showing the dependence the latter have on the former.

In the diagram of curves which is formed from Table A., the abscissæ represent the days of the month, from the 1st of November to the end of December 1848; the ordinates in the upper half of the diagram the observed mean level of the ocean, and in the lower half the corresponding mean height of the barometer on each day during that period.

TABLE A.

Date. 1848.	Observed level.	Observed Barom.
	ft. in.	inches.
Nov. 1.	20 9·9	30·101
2.	21 4·4	29·683
3.	21 8·3	29·351
4.	21 3·5	29·643
5.	20 9·7	30·168
6.	20 8·1	30·270
7.	20 9·2	30·123
8.	21 0·4	29·756
9.	21 0·4	29·706
10.	21 0·7	29·759
11.	20 10·0	29·894
12.	20 11·7	30·064
13.	20 6·4	30·225
14.	20 11·2	30·047
15.	20 10·7	30·185
16.	21 1·0	29·957
17.	21 2·1	29·727
18.	21 1·2	29·780
19.	21 0·2	29·753
20.	21 0·5	29·703
21.	20 9·8	29·847
22.	21 2·3	29·953
23.	20 11·2	29·937
24.	21 0·2	29·896
25.	21 0·0	29·889
26.	21 1·3	29·936
27.	21 0·5	29·830
28.	20 11·6	29·773
29.	21 1·5	29·733
30.	21 1·1	29·903
Dec. 1.	21 1·9	29·957
2.	21 1·2	30·002
3.	21 1·5	29·938
4.	21 1·3	29·843
5.	20 10·6	29·792
6	20 8·1	30·001
7.	20 7·7	30·121
8.	20 11·9	29·903
9.	21 2·0	29·766
10.	20 10·6	29·905
11.	20 11·0	29·879
12.	20 11·6	29·887
13.	21 1·0	29·887
14.	21 3·6	29·790
15.	21 4·5	29·718
16.	21 2·4	29·837
17.	20 10·7	30·052

TABLE B.

Date. 1848.	Observed Barom.	Observed level.	Correc-tions.	True level.	Remarks.
	inches.	ft. in.	inches.	ft. in.	inches.
Nov. 6.	30·270	20 8·1	+5·24	21 1·34	Barom. .....30·227
Nov. 13.	30·225	20 6·4	+4·64	20 11·04	ft. in.
Nov. 15.	30·185	20 10·7	+4·11	21 2·81	Level .....20 8·4
Nov. 5.	30·168	20 9·7			Correction ... +4·66
Nov. 7.	30·123	20 9·2		3·19	Corrected level...21 1·06
Dec. 7.	30·121	20 7·7	Mean ...	21 1·06	
Nov. 1.	30·101	20 9·9			
Nov. 12.	30·064	20 11·7			
Dec. 17.	30·052	20 10·7			
Nov. 14.	30·047	20 11·2			
Dec. 2.	30·002	21 1·2			
Dec. 6.	30·001	20 8·1			
Nov. 16.	29·957	21 1·0			
Dec. 1.	29·957	21 1·9			
Nov. 22.	29·953	21 2·3			
Dec. 3.	29·938	21 1·5			
Nov. 23.	29·937	20 11·2			
Nov. 26.	29·936	21 1·3			
Dec. 10.	29·905	20 10·6			
Nov. 30.	29·903	21 1·1			
Dec. 8.	29·903	20 11·9			
Nov. 24.	29·896	21 0·2			
Nov. 11.	29·894	20 10·0			
Nov. 25.	29·889	21 0·0	.....	.....	
Dec. 12.	29·887	20 11·6	.....	.....	
Dec. 13.	29·887	21 1·0	.....	.....	inches. Barom. .....29·867
Dec. 11.	29·879	20 11·0	.....	.....	ft. in.
Nov. 21.	29·847	20 9·8	.....	.....	Level.....21 0·16
Dec. 4.	29·843	21 1·3	.....	.....	
Dec. 16.	29·837	21 2·4	.....	.....	
Nov. 27.	29·830	21 0·5			
Dec. 5.	29·792	20 10·6			
Dec. 14.	29·790	21 3·6			
Nov. 18.	29·780	21 1·2			
Nov. 28.	29·773	20 11·6			
Dec. 9.	29·766	21 2·0			
Nov. 10.	29·759	21 0·7			
Nov. 8.	29·756	21 0·4			
Nov. 19.	29·753	21 0·2			
Nov. 29.	29·733	21 1·5			
Nov. 17.	29·727	21 2·1			
Dec. 15.	29·718	21 4·5			
Nov. 9.	29·706	21 0·4			
Nov. 20.	29·703	21 0·5			
Nov. 2.	29·683	21 4·4	−2·53	21 1·87	inches. Barom. .....30·559
					ft. in.
Nov. 4.	29·643	21 3·5	−3·05	21 0·45	Level .....21 5·4
Nov. 3.	29·351	21 8·3	−7·02	21 1·28	Correction ... −4·17
Mean ...	29·874	21 0·21		·60	Corrected level..21 1·23
			Mean ...	21 1·2	

The result of these forty-seven days of hourly observations gives for the mean height of the barometer 29·874 inches, and the mark of the mean level of the ocean 21 feet 0·21 inch.

In order to avoid the effects of accidental irregularities, the means of the three days of greatest and of least pressure are taken to compare with the mean level of

the ocean on the corresponding days, and from the difference of the pressures and the difference of the levels to determine the relation of each to the other.

	inches.		ft.	in.
The mean of three days' greatest pressure was	30·227	Of corresponding level	20	8·4
The mean of three days' least pressure was.....	29·559	Of corresponding level	21	5·4
Difference.....	·668	Difference.....		9·0

Thus a difference of pressure equal to ·668 of an inch in the barometer, produces a difference of 9 inches in the mean level of the ocean, from which we can of course readily compute the exact relation of cause and effect. Thus the difference of level, 9 inches, divided by the difference of pressure 0·668 of an inch, equals 13·467. The effect, therefore, of the pressure of the atmosphere on the level of the ocean is 13·467 times greater than the effect it produces on the mercury in the barometer, or very nearly in the inverse ratio of the specific gravity of the two bodies; that of the sea-water being 1·026, and that of mercury 13·566, or as 1 to 13·224.

This remarkable coincidence of the results must, however, in this case be considered in a great measure accidental, for if instead of the three days' greatest and least pressure we were to take seven days of each, from which a better result might be expected, we find, instead of the ratio being as 1 to 13·467, it would by these means become as 1 to 12·562; and if we take the mean of twelve highest and twelve lowest barometers, the ratio would be still further reduced as 1 to 11·60; but these differences in the result are chiefly caused by the evident irregularities of the mean level on the 9th and 20th of November, occasioned by a heavy gale of wind, in each case of two days' continuance. This circumstance, although accounted for in this particular instance, seems to indicate the necessity of multiplying observations of this nature before exact results can be determined.

I may here remark, that the effect produced appears from these observations to be strictly uniform in its progression from the greatest to the least pressure. By combining the mean of the three days' observations of next greater and three days of less pressure with that nearest to the mean pressure for the whole period, we find the result corresponds nearly with the mean pressure, and the ratio between the extremes almost equal; thus, on December 11, the mean pressure was 29·879, differing very little from the mean of the whole period; and the three days' observations above and below combined with it, give a mean of 29·867, the corresponding mean level of the seven days being 21 ft. 0·16 in., which so closely approaches that of the whole period, that they may be deemed identical, and would tend to show that the effect from the greatest to the mean pressure, and from the mean to the least pressure, is in strict progression. It is not possible, however, from so limited a number of observations, to determine this point with certainty, or to attempt any intermediate inferences.

We have, from these observations, been able to deduce results which plainly point to the law which governs the effect of the pressure of the atmosphere on the

mean level of the ocean, and may be encouraged to pursue the investigation through a more extended series of observations, in order that we may at length arrive at the most accurate conclusion that the observed facts may justify.

For all practical purposes, it may in the mean time be well to assume, what the preceding observations seem to indicate, that the ocean is a water barometer on a vast scale of magnificence, and that the level of its surface is disturbed by every variation of atmospheric pressure, inversely as the mercury in the barometer, and exactly in the ratio of the relative specific gravities of the water and the mercury. And as all observations of the tides, before they can be safely employed to investigate the laws by which they are governed, should in the first place be corrected for the large and hitherto mysterious irregularities which the variations in the pressure of the atmosphere produce, the following formula may be used to determine the correction z to be applied to all observations of the height of the tide, or the mean level of the ocean deduced from them, to reduce them to the mean pressure of the atmosphere.

$$(1)\ z=(B-\beta)D, \text{ or } (2)\ L=\lambda\pm(B-\beta)D,$$

positive when β is greater than B, and negative when less.

In which B denotes the mean pressure of the atmosphere.

L the correct height of the tide or mean level of the ocean.

D the relative specific gravity of sea-water and mercury.

λ the observed height of the tide or observed level of the ocean.

β the corresponding height of the barometer.

And if we assume B=29·874 inches, the mean of the preceding observations; L=21 ft. 0·21 inch, the mean of the preceding observations; and D=13·224, we can readily compute the correction z to be applied to any observed tide, having the corresponding height of the barometer. For example, on the 3rd November the mean barometer for the day was β 29·351 inches, and the corresponding mean level of the sea λ=21 ft. 8·3 inches; then $B-\beta\times D=-6{\cdot}92$, which applied to λ= 21 ft. 1·38 inch; and on the 13th November the mean barometer was β 30·225 inches, and the corresponding observed level λ=20 ft. 6·4 inches; again, $B-\beta\times D=+4{\cdot}64$ added to λ=20 ft. 11·04 inches.

On these two days the observed level of the ocean differed no less than 14 inches; but by the application of the correction found by the above formula, the observed level in each day is brought to agree with the true mean level to little more than 1 inch. I may further observe, that much greater irregularities are to be hereafter noticed in the more extensive series of observations which followed this, and by the same formula are capable of being reduced to an equally near accordance with the mean level, as deduced from the whole of the observations.

Thus it is evident that one of the many causes of the apparent irregularities of the tides (and at Port Leopold certainly the greatest of all) is clearly traceable to a well-established and invariable law.

Postscript.

When this paper was drawn up some years ago I was ignorant of the researches of M. Daussy on the same subject, or the confirmation of his discovery by Sir John Lubbock, whose valuable treatise on the Tides having been long out of print is, unfortunately, too little known to naval officers. Dr. Whewell directed my attention to it when I mentioned to him the result of my deductions from the observations at Port Leopold, and although the investigations of these eminent philosophers relate only to the effect of the pressure of the atmosphere on the height of high water, and differ widely in their results, owing to the localities in which the observations were made being unfavourable for the detection of the universal law which governs the amount of apparent irregularities, I have extracted from Sir John Lubbock's work a paragraph which clearly shows the exact state of the question previous to my investigations. He says, p. 48, "M. Daussy has ascertained that at Brest the height of the high water varies inversely as the height of the barometer, and that the British Channel there rises more than 8 inches for a fall of about half an inch in the barometer. I have found that at Liverpool a fall of a tenth of an inch in the barometer corresponds to a rise in the River Mersey of about an inch, and that at the London Docks a fall of one-tenth of an inch in the barometer corresponds to a rise in the River Thames of about seven-tenths of an inch. So that with a low barometer the tides may be expected to be high, and *vice versâ cæteris paribus*."

Thus M. Daussy found the height of high water to be affected

At Brest in the ratio of	1 : 16
Sir John Lubbock at Liverpool . . .	1 : 10
And at London	1 : 7

The results of their investigations at these three places differed so much from each other, that their practical application became limited to the correction of the height of high water at the places where the observations were made.

The result of the deductions from the observations at Port Leopold is, I have no doubt, of more universal application in all harbours where the ocean has free ingress and egress, as a comparison with the extensive series of tidal observations made at New Zealand, Cape Horn and the Falkland Islands, during my voyage to the Antarctic Seas in 1839 to 1843, tends to show. But the subject is well worthy of investigation in other localities, as doubtless a different ratio will be found to obtain in proportion as the ingress of the waters of the ocean is free, or obstructed by narrow channels or sand-banks.

J. C. R.

Aston-Abbott's House, Aylesbury,
November 6, 1854.

XIII. *On the frequent occurrence of Indigo in Human Urine, and on its Chemical, Physiological, and Pathological Relations. By* ARTHUR HILL HASSALL, *M.D. Lond., Member of the Royal College of Physicians, Physician to the Royal Free Hospital, &c. &c. Communicated by Professor* SHARPEY, *Sec. R.S.*

Received June 10, 1854,—Read June 15, 1854.

SINCE I had the honour of communicating to the Royal Society in June last *, the results of my investigations on the frequent presence of indigo in human urine, I have continued to follow up the subject, and this, I trust, with some interesting and important results.

First. After some difficulty, I have succeeded in obtaining the blue pigment in question in considerable quantity, so as to allow of its being subjected to further experiment, with the view of furnishing additional proofs of its being really indigo; and second, I have succeeded in determining the cases in which this pigment occurs most frequently and abundantly, and its probable source.

The present communication comprises these additional particulars and observations, together with the chief facts connected with the occurrence of indigo in the urine which have resulted from my previous investigations.

Remarkable cases of variously-coloured urine have been described from time to time; such instances have, however, hitherto been supposed to be of extremely rare occurrence, more than a single example of the kind but seldom falling under the observation of any one individual; they have also been regarded rather as curiosities and extraordinary anomalies, than as physiological and pathological facts, which, if rightly understood, are full of the deepest interest and importance.

Although several cases of coloured urine have been described, two only, in which the colouring matter has been at all satisfactorily proved to be indigo, have been recorded.

The circumstances which led to the investigations recorded in this communication were the following:—Some four or five years ago, when examining urinary deposits under the microscope, I frequently noticed in the field of vision, particles of a deep blue colour. So often did this occur, that I could not even then help suspecting that their presence could scarcely be accidental; however, no analysis of the blue colouring matter was at that time made, and the circumstance was in a fair way of being forgotten, until the recollection of it was renewed by another occurrence.

In June 1852, a sample of urine freely exposed to the air in an open vessel, was

* See Proceedings of the Royal Society, June 16, 1853.

observed after four or five days' exposure gradually to change colour; the pellicle or scum which had formed on the surface of the urine became at first slate-coloured, and at length deep blue, with here and there a rusty-red tint: the urine also underwent, at the same time, some remarkable changes, becoming thick and turbid, deep brown, greenish, bluish-green, and finally of a faded yellowish-green colour; a considerable sediment was found at the bottom of the glass, this was deep brown, soft and deliquescent, intermixed with a little blue colouring matter, and it had a medicinal smell resembling somewhat that of valerian.

In this state, without undergoing any further material changes, the urine remained for many days.

Examined with the microscope, the scum or pellicle on the surface was found to consist of Vibriones, innumerable animalcules, and crystals of triple phosphate, with a great many fragments and granules of a deep and bright blue colour.

So remarkable and striking was the appearance presented by this urine, that I could not help fancying a mistake must have occurred, and that possibly some foreign colouring matter had accidentally found its way into the urine; I therefore procured a second sample of the same urine, taking every precaution to avoid fallacy, and keeping it in a room to which no one had access but myself. Gradually the same changes ensued as in the first sample, and this likewise became blue.

Having thus ascertained that the changes observed were due to something contained in the urine itself, I next proceeded to set aside in open vessels a series of urines, all from the same patient, noticing the alterations which occurred from day to day.

The first urine of the series, when passed, was somewhat alkaline to test-paper, had a specific gravity of 1017, and was of a light brown colour; there formed on its surface, in the course of three or four days, a thick, greasy-looking, soft scum, consisting of Vibriones and very many large and fine crystals of triple phosphate; at about this time the scum became greyish-blue, lavender, bright blue, and finally, after four or five days more, of a deep indigo-blue colour, which was permanent. When disturbed or broken, the blue crust usually turned, after some hours, rusty-red at the broken or fissured part, but gradually the original blue colour was restored. The urine itself at the same time underwent some singular changes; it became thick, brown, green, bluish-green, and finally nearly black. As evaporation took place, the blue crust became attached to the sides of the vessel, and on pouring the urine into another glass, there was found a considerable quantity of a brown, extractive-like substance at the bottom of the vessel, mixed with some of the blue colouring matter which had fallen from the surface of the liquid.

In the second urine of the series the changes were similar in kind, but less in degree. This urine was alkaline, of specific gravity 1015, and the pellicle of Vibriones, animalcules and triple phosphate which formed on the surface became gradually coloured as before, being first slate-coloured, then bluish, and lastly light blue. The

urine in this sample became thick and of a dirty grass-green colour, and a similar brown deposit with some blue colouring matter was found at the bottom. Some of the blue and brown deposits from this and the previous sample were collected and subjected to analysis.

The third, fourth and fifth samples resembled very closely the second, but contained less of the blue and brown colouring matters.

The sixth sample was neutral, of specific gravity 1007, and contained rather much vaginal epithelium. A pellicle gradually formed, limited principally to the borders of the fluid; this became of a decided bluish tint, the urine itself at the same time becoming dark brown, letting fall a deposit of the same colour, and possessing the same characters as in the other samples. Examined with the microscope, pieces of the blue colouring matter were detected in the scum, as well as triple phosphate, Vibriones, and a few of the animalcules.

The seventh urine was decidedly alkaline, of specific gravity 1019, and contained much mucus and epithelium; eight days afterwards, a scum, which had become *deep blue*, had formed around the margin of the fluid; the urine had changed from light brown to a dark greenish tint, and was very thick, some of the brown sediment present in the other samples being found at the bottom of the glass.

The eighth urine was of a straw-colour, slightly acid, of specific gravity 1015, and contained much mucus and epithelium; at the end of eight days, the scum, which had formed chiefly around the edge of the fluid, was *perceptibly blue* on one side only, but the colour was neither so deep nor so extensive as in the previous sample. The urine itself became dark and thick.

The ninth sample was decidedly acid, of specific gravity 1009, and contained albumen, many blood-corpuscles, and much mucus. The pellicle which formed around the edge of the fluid did not become in the least blue, neither did the urine undergo any very considerable change of colour, although it became a few shades deeper.

The tenth sample was slightly acid, also of specific gravity 1009, and contained much epithelium, but no albumen. A thick scum of Vibriones and animalcules collected after a time over the entire surface, but it did not become at all blue; the urine was only a few shades deeper coloured than when passed. No blue particles were discovered with the microscope.

I will now proceed to state the results obtained by the chemical examination of the urine, the blue colouring matter, and the brown extractive, as made by Dr. Letheby and myself. The analysis of the urine was made after it had been standing for some time, and after it had been shaken and disturbed, its appearance being considerably altered thereby.

The Urine.—The urine of the second sample at the time of analysis, when shaken up, had a dark greenish-brown colour, was strongly alkaline both from fixed and volatile alkalies, and emitted a highly ammoniacal odour. It was turbid from the presence of a large quantity of triple phosphate, as also from the colouring matter;

these quickly subsided and left a clear supernatant liquid of a deep wine-red colour; above the deposit of earthy phosphates, collected at the bottom of the vessel, the colouring matter formed a thin stratum composed of dirty bluish-green flocculi.

The bottle was corked and set aside for ten days, at the end of that time the bluish-green precipitate had entirely disappeared, but on removing the cork and allowing free access of atmospheric air for some days, the coloured deposit was again produced. While in this state the liquid was filtered and the precipitate washed with water, then drenched with weak hydrochloric acid, and finally dried. By this means a rich blue precipitate was obtained possessing the following characters, chemical and general.

α. It exhibited a coppery lustre on being rubbed with the nail.

β. It presented an amorphous, granular and fragmentary appearance under the microscope.

γ. It was not soluble in water, dilute acids, ether, alcohol, or turpentine; nor was it affected by spirits of wine in which there was a little free acid.

δ. It was not attacked by liquor potassæ at ordinary temperatures, but when heated therewith, it was converted into a dirty, yellowish-brown solution.

ε. It was freely dissolved by strong sulphuric acid, and produced a deep blue liquid miscible with water, and which chlorine had the power of bleaching.

ζ When heated with fuming nitric acid, it yielded a greenish-yellow solution, which became of a brilliant yellow with liq. potassæ.

η. On diffusing it through water and boiling with lime and grape-sugar, it furnished a wine-red fluid, which on being filtered and then neutralized with hydrochloric acid, gave a greenish-blue precipitate. Another portion of the liquor was exposed to the air for a few hours, and it reacquired its blue colour.

θ. When heated in a test-tube it evolved vapours of a rich violet-red colour, and produced the characteristic odour of sublimed indigo.

The urine that was filtered off from the above precipitate was allowed to evaporate spontaneously, by which means it yielded an additional quantity of indigo, which adhered in the form of very small flakes to the sides of the dish. It also gave a rather large proportion of a deliquescent brown colouring matter, and a number of large rhombic plates of ammoniacal phosphate of soda and potash. These crystals were removed from the vessel by means of a needle, and the brown residue was treated first with alcohol and then with water. The alcohol acquired a deep brownish-red colour, and the water a dark brownish-green. Both of these solutions were evaporated at a temperature of 160° Fahr.

The alcoholic solution furnished a rich brown extractive, which was soluble in water, but not in dilute acids; and nitric acid did not produce that play of colours which is characteristic of bile pigment, nor did the precipitate formed with basic acetate of lead furnish a purple liquid with alcohol and free acid. A strong solution of potash dissolved the extractive and yielded a deep blood-red fluid, which was

rendered green and opalescent by boiling. These reactions show that the brown pigment was somewhat like hæmatin in its chemical manifestations.

While the aqueous solution of the colouring matter was undergoing evaporation, it gave a further supply of indigo, which was formed most freely at the edge of the liquid. The residue was made black by concentrated sulphuric acid and deep brown by potash.

The blue colouring matter.—The two samples of this, when subjected to analysis, were in a dry state, and were mixed with a large quantity of earthy phosphates, Vibriones, mucus and epithelium; one of them gave a dark brown solution with concentrated sulphuric acid, and the other a dirty blue. Both of these solutions were decomposed by water, furnishing in the former case a dark brown deposit, and in the latter a dirty green. In their other reactions, however, they presented the characters of indigo; and it is especially deserving of notice that they were reduced by lime and grape-sugar, giving a liquid from which hydrochloric acid threw down a greenish-blue precipitate.

The cause of concentrated sulphuric acid giving with one of these samples a brown solution, and with the other only a dirty blue, was, no doubt, mainly owing to the large quantity of animal matter, mucus, Vibriones and epithelium with which the specimens were contaminated. The acid, from its charring effect on this, would produce a brown or blackish solution, thus obscuring the colour of the solution of sulphate of indigo.

The brown extractive.—The brown extractive yielded nearly the same results as on its first analysis, when deposited on the evaporation of the filtered urine; and the aqueous solution, as before, furnished a few blue flocculi. A portion of the alcoholic extract was treated with potash, for the purpose of ascertaining whether it contained leucine; and the product, on the addition of hydrochloric acid, gave off a powerful odour, which was somewhat like *valerianic acid*, but the result was too doubtful to be of much value. I have already referred to the peculiar smell of valerian emitted by the extractive of more than one of the samples.

We have thus then obtained tolerably conclusive evidence that the blue colouring matter in this case was indigo.

It was not very long after the occurrence of the first case of blue urine that other cases fell under my observation.

To the second case, as to the first, I was led by accident. A sample of urine left for some days exposed to the air gradually changed colour, the urine turning bluish-green, and its surface becoming covered with a bluish scum. As before, a series of samples of this urine was set aside, the changes which ensued being noticed from time to time.

The specific gravity and reaction of the first sample of urine set aside, were not taken at the time it was passed. After it had been exposed to the air for about ten days, the following was found to be its condition. An irregular and broken scum

had formed upon the surface; this consisted chiefly of very much triple phosphate, of Vibriones, numerous crystals of phosphate of lime, and one small circular tuft of the fungus *Penicilium glaucum* in perfect fructification; in the centre of the glass was a large patch of phosphatic pellicle, an inch and a half in diameter, rusty-red at the edges, but decided blue in the centre; a rim or border of blue had likewise collected around the edges of the fluid; lastly, the urine had become very deep brown, with brown extractive at the bottom of the glass.

The second sample, passed after a severe attack of vomiting, was slightly acid only, of specific gravity 1014, and was of a straw-colour; it changed colour very rapidly, becoming dark brown; a phosphatic pellicle soon formed over the entire surface, which became first slaty-blue, and then decidedly blue; the urine also quickly changed colour, becoming dark brown, while at the bottom of the glass there was a large quantity of the brown, treacly-looking extractive.

The third sample was neutral, of a light brown colour, and of specific gravity 1012; after three or four days it became covered with a greasy, iridescent, phosphatic pellicle, which gradually turned slaty-blue, especially around the edges of the fluid, which was thickish and brown. Under the microscope many pieces of the blue colouring matter were detected.

The fourth sample, obtained many days subsequent to the above, differed greatly from the others in its acid reaction and in its greater specific gravity. It was very decidedly acid, rather high-coloured, and of specific gravity 1024. In the course of a few days small circular patches of *Penicilium glaucum*, in perfect fructification, were observed studding the surface of the urine; in the intervals between these patches, and surrounding them, was a phosphatic pellicle; the urine had now become alkaline, turbid and deep brown, no blue being visible to the naked eye; but on tearing up one of the tufts with needles, and examining it under the microscope, numerous blue, indigo-like masses were seen, as well as threads of the sugar-fungus, showing that a small quantity of sugar was present in this urine.

Several other samples of this urine were examined; these changed colour a good deal, becoming turbid and brown, and more or less blue being detected; sometimes the blue was visible either on the surface or around the edges of the urines; in others the microscope was necessary for its discovery.

The urine, the blue deposit, and the brown extractive of the first of the above samples were likewise subjected to chemical analysis. The results were similar to those obtained in the previous case, the blue colouring matter possessing all the characters of indigo.

More recently, a third very decided case of blue urine has fallen under my observation. A bottle of urine was received from my brother, Dr. Hassall, of Richmond, on the 26th of April 1853, labelled "Mr. Arters, obscure case." I examined this at the time without being able to discover anything very wrong about it; it was pale, slightly acid, of specific gravity 1013, and it let fall a large quantity of a mucus-

like deposit, which was more than an inch in depth in a six-ounce bottle. Examined with the microscope, no crystalline deposit of any kind was discovered; the bottle was kept corked until May 21, the urine undergoing no particular change during the interval, but only getting a little deeper-coloured. On that date it was poured into a glass; by the 24th the urine had changed colour greatly, and a good deal of blue, visible to the naked eye, had formed upon the surface. On the following day the surface had become deep indigo-blue all over, and the urine was thick and of a dull grass-green colour; some of the blue colouring matter had become deposited upon the layer of mucus at the bottom of the glass, but there was no sediment of brown extractive. On the 26th the fluid had become more bluish-green, and was very deep-coloured; it also contained triple phosphate, Vibriones, and the usual animalcules. By the 28th much of the blue matter had fallen as a deposit, and the liquid had become brownish-green; a day or two later it was tawny brown; the blue colouring matter which had not subsided as a deposit, adhered to the sides of the glass, forming a broad, deep blue ring round its circumference. This urine was chiefly remarkable for the extraordinary rapidity with which it changed colour, and with which the blue colouring matter was developed. The changes were so rapid, that every hour was observed to make a considerable difference in the appearance and characters of the urine. This is possibly explained by the supposition, that while in the corked bottle, the substance afterwards developed into blue indigo had undergone a certain amount of change through the limited access of oxygen.

Chemical analysis proved that in this case likewise the colouring matter possessed the usual characters of indigo; it gave a blue solution with sulphuric acid, was decolorized by chlorine and nitric acid, and it sublimed in violet-red vapours when heated in a test-tube *.

I have now to observe that I have detected the presence of indigo in human urine in a variety of other cases besides the above, of all which I have preserved memoranda. In some the quantity of indigo was, as in the three examples above referred to, very considerable; the urine in some of them was coloured with it, or a deep blue pellicle formed on the surface. In many of the remaining cases, on the other hand, the quantity was less considerable; the scum on the surface was only slightly coloured, or the quantity was so small as to require the microscope for its detection. In nearly all of these instances the blue colouring matter was subjected to analysis; where the amount was so small that it could only be detected by the microscope, it was tested by reagents, such as sulphuric acid, liquor potassæ, &c., applied while the blue fragments were under the object-glass of the microscope.

Where the urine was high-coloured and acid, and where the quantity of the blue colouring matter was but small, I have observed it to be deposited in the threads of the thallus of the fungus *Penicilium glaucum*, forming patches which to the eye

* A portion of the blue pigment formed in this case accompanied my previous communication to the Royal Society.

appeared black; but the colouring matter contained in which, was, under the microscope, seen to be of a deep blue.

In order that a doubt might not remain as to the blue colouring matter described in the present communication being really indigo, it had been suggested to me that it was highly desirable to collect it in sufficient quantity to allow of its conversion into aniline.

With the above view, I set aside upwards of twenty urines obtained from a variety of different cases of disease, watching them from time to time. In four of these the blue substance was formed in considerable amount; it was carefully collected, and subjected, both by Dr. Lethery and myself, to the following process of analysis.

First. It was purified by steeping it for several days in dilute hydrochloric acid, by which means the phosphates, chlorides and urea were dissolved out, and the residue, when dried, had a brighter blue colour.

Secondly. It was tested as follows:—

α. When heated it sublimed in purple vapours; and on further application of heat it evolved empyreumatic vapours, which possessed the properties of aniline and the odour of burnt indigo.

β. When treated with sulphuric acid, it furnished a blue solution, which was not destroyed by dilution with water, but was bleached by chloride of lime.

γ. When boiled with dilute nitric acid and evaporated to dryness, it yielded a dirty orange-yellow material (isatine), which, when subjected to heat and the action of potash, gave an alkaline volatile fluid, and this, when tested with a solution of chloride of lime and with a piece of deal moistened with hydrochloric acid, furnished the characteristic reactions of aniline.

Aniline was likewise procured by the simple distillation of the pigment with a concentrated solution of caustic potash, as shown by the development of the well-known violet-blue colour on the addition of a solution of chloride of lime.

We have, in the next place, to consider the important question of the source and origin of indigo in urine.

We have seen that blue indigo is not usually present in urine when first passed, and in which it afterwards makes its appearance, but that it is gradually formed some time subsequently, on exposure to the atmosphere, by a process of oxidation. One or two cases scarcely admitting of a doubt, are, however, recorded, in which coloured indigo has been voided with the urine.

We must not conclude, from the absence of coloured indigo in fresh urine, that that substance was not present in the urine in a modified form when first voided, since there is a colourless or white indigo, which, in contact with oxygen, undergoes precisely the same transformations as those through which the blue indigo of the urine was observed to pass; changing, like it, from slaty-blue to light, and ultimately to deep blue.

Whether the blue indigo of the urine is derived directly from white indigo, or

from some other substance, as urine-pigment, capable of being transformed into blue indigo, it is not easy to determine. It is most likely, however, that the formation of white indigo in all instances precedes that of blue, but it is uncertain whether the white variety is voided with the urine, or whether it is formed from some substance contained in that fluid subsequent to its elimination. The fact, however, that blue indigo is in some cases immediately developed on the addition of hydrochloric acid to recent urine, appears to show that white indigo is present in the urine when first voided.

It is at all events certain that a very close relation exists between indigo, whether colourless or coloured, and two animal products, namely hæmatin and urine-pigment; and there is much reason for believing that in many of the present cases the indigo was formed either from modified or altered hæmatin or urine-pigment, since some of the analyses show that blue indigo was freely developed from the aqueous solution of the brown extractive, which itself was found so nearly to resemble hæmatin in its chemical manifestations. The close relation which exists between hæmatin and indigo is shown by the following elementary analysis of these substances :—

	Hæmatin (Mulder*).	White indigo (Caum).	Blue indigo (Caum†).
Carbon	70·49	72·72	73·22
Hydrogen	5·76	4·54	2·92
Nitrogen	11·16	10·60	11·26
Oxygen	12·59	12·12	12·60

Or, if the relation be exhibited in another way, it will be seen that there is a difference of only four atoms of carbon and four of hydrogen between the composition of three atoms of indigo and one of hæmatin—

1 Hæmatin $= C^{44} H^{22} N^3 O^6$.

3 Indigo $= C^{48} H^{18} N^3 O^6$.

Again, leucine is a common product of the decomposition of organic, or rather of albuminous matters, and it was thought that this body was present in the alcoholic extractive; if so, the relation between hæmatin and indigo is still more remarkable; for, as suggested by my friend Dr. Letheby, to whom I am much indebted for the aid afforded in these analyses, one equivalent of hæmatin and two of water contain the elements of two atoms of indigo and one of leucine. The relation stands thus:

	C.	H.	N.	O.			C.	H.	N.	O.
1 Hæmatin .	44	22	3	6	=	2 Indigo .	32	12	2	4
2 Water . .		2		2		1 Leucine .	12	12	1	4
	44	24	3	8			44	24	3	8

It is therefore not difficult to imagine that a transmutation of hæmatin into indigo may be effected under certain circumstances both within and without the system.

* Journ. für Prakt. Chem., bd. 28. s. 340.

† Annals of Philosophy, 2nd ser. vol. lxxxii.

Since, however, normal urine-pigment very closely resembles hæmatin in its composition, it is probable that in some cases indigo is formed from this pigment, altered or modified by disease.

Professor Scherer* long since directed attention to the fact, that there is a close relation between the elementary composition of hæmatin and the several colouring matters of bile and urine, and he even hazards a conjecture that the two latter may be derived from the former. If we view the per-centage composition of all these substances side by side, the following is the aspect they present:—

	White indigo (Crum).	Hæmatin (Mulder).	Bile-pigment (Scherer).	Blue pigment of urine (Scherer).	Brown pigment in disease. (Scherer).	Brown pigment in health (Scherer).
Carbon	72·72	70·49	68·19	66·99	61·65	58·43
Hydrogen	4·54	5·76	7·47	5·95	5·60	5·16
Nitrogen	10·60	11·16	7·07	7·12	7·29	8·83
Oxygen	12·12	12·59	17·26	19·94	25·46	27·58

These numbers not only indicate the relation which exists between these substances, but they also show that there is a progressive removal of carbon by oxidation, and it is probable that the last of the series may represent the form in which, under ordinary circumstances, the hæmatin of the blood is removed from the body.

To the above list of colouring matters, all intimately connected by their elementary composition, may be added melanin, itself supposed to be derived from bile-pigment, and the composition of which, according to Scherer†, is as follows:—

Melanin.

Carbon	58·084
Hydrogen	5·917
Nitrogen	13·768
Oxygen	22·231
	100·000

In the cases related in this paper, no reason exists for supposing that the indigo was derived from the colouring matter of bile, as in the urines in which the indigo was found, no traces of the presence of that secretion could be discovered, while in one only of three samples of urine examined highly charged with bile was any indigo found, and then but in small quantity.

The colour and characters of the urines, as well as their chemical analysis, favour the supposition that the indigo, whether white or blue, was derived either from altered hæmatin or urine-pigment. The urines in which the indigo occurred in the largest quantities were pale, straw-coloured or light brown, often somewhat turbid, and appeared as though but imperfectly elaborated.

* Ann. der Chem. und Pharm., bd. 57. s. 181–195.

† *Ibid.* 40. s. 6.

I have employed the phrases "altered hæmatin" or "urine-pigment," because it does not appear that, by any treatment of the urine with reagents, indigo can be developed in healthy urine at will. I have made several attempts with this view, rendering various healthy urines alkaline (since the largest quantity of indigo was always found in alkaline urines) with potash, soda, lime-water, &c., but without obtaining any definite result.

Reviewing the whole of the cases which have fallen under my observation in which indigo has become developed in the urine, there is every reason to believe that the occurrence of that substance in the urine is strictly pathological: that it is so when in large amount, no doubt whatever can be entertained. Looking to the composition of indigo, there is also no doubt that, like bile and urine pigments, it forms a vehicle for the elimination of carbon from the system; and since it contains a much larger proportion of carbon than either hæmatin, urine or bile pigments, we should be led to look for its occurrence in the urine in all those cases of functional derangement of any kind in which any impediment exists to decarbonization, as is the case especially in most diseases of the organs of respiration.

From the facts which I have already succeeded in ascertaining, there is good reason for believing that the above view is, in the main, correct. Turning to the history of the three cases of blue urine which first attracted my attention, I find that one died phthisical; the second, though living, has undoubtedly tubercular disease of the lungs, with greatly diminished capacity of respiration; while in the third case there have been evidences, although less marked, of lung affection.

Again, turning to the histories of the twenty cases in which samples of urine were set aside for observation, and in four of which samples indigo became developed in considerable quantity, I find that these were also cases of phthisis. These facts possess the greatest interest, and appear to point clearly to the causes which determine the presence of indigo in the urine.

From other observations not yet completed, it appears, however, that indigo is not developed in the urine in all cases of phthisis. If the urine voided be very acid, or if the affection of the lungs be of but trifling extent, no great development of that substance will take place. Neither, on the other hand, is the occurrence of indigo in the urine by any means limited to cases of phthisis, as it may occur in abundance in any case, no matter from what cause it proceeds, in which there exists great impediment to the elimination of carbon from the system, as in scarlatina, Bright's disease, cholera, &c.

Indigo is not the only blue colouring matter which has been stated to occur in urine, since two or three others have been described by different observers, as ferrocyanide of iron or prussian blue, cyanourine and uroglaucin. I now propose to contrast the two last of these with blue indigo.

Prussian blue may of course be readily distinguished from indigo, and it would

appear that the tests, as laid down in books, for cyanourine are scarcely less distinctive*.

Cyanourine is described as a dark blue powder, destitute either of taste or odour; it is scarcely soluble in water, moderately so in boiling alcohol (the solution being blue), but it is deposited on cooling. It is dissolved by dilute acids, the solution being brown or red, according to the quantity of acid. With sulphuric acid a brown liquid is formed, which on evaporation leaves a residue of a carmine colour soluble in water; it is precipitated from its acid solution by ammonia, lime-water, and by the fixed alkalies. It gives a brown solution with nitric acid, and like indigo, is converted into nitropicric acid. It is said to be principally distinguished from indigo by its forming a reddish-brown solution with sulphuric acid, and by not subliming, when heated, in a test-tube. Urine containing cyanourine is of a blue colour, the colouring matter on repose falling as a sediment.

Heller† applies the term *uroxanthin* to the colouring principle or material of the urine; and that of *uroglaucin* to a blue pigment which he considers to be developed from *uroxanthin* under the influence of disease. This pigment, dried, forms a powder of a coppery lustre resembling indigo, and dissolves in alcohol with a splendid purple colour; its occurrence is said to be especially frequent in Bright's disease.

According to Heller, cyanourine is simply a mixture or combination of *uroglaucin* and *urrhodin*, and both these latter are but the products of *uroxanthin*, the colouring matter of healthy urine.

It would appear, therefore, that there are no very essential differences between *cyanourine* and *uroglaucin*, while there are so many points of resemblance between them both and indigo, that one is led strongly to suspect that they are simply some condition or modification of indigo. Not only do these substances agree in many of their chemical reactions with indigo, but they also very closely resemble it in their ultimate composition.

Great care should be taken to obtain these blue deposits in as pure a state as possible for analysis, for being in general found in alkaline urines, they are very apt to be contaminated with large quantities of animal matter, Vibriones, triple phosphate, &c. The presence of the animal matter obscures the action of concentrated sulphuric acid on indigo, it being charred by that reagent, and a reddish-brown solution is formed instead of a blue one. It also interferes with the sublimation of the indigo and the elimination of the characteristic vapours, as also with its conversion into aniline; lastly, indigo as well as cyanourine frequently furnishes a blue solution when boiled with alcohol. I cannot help therefore considering it to be highly probable that the blue pigments which have been set down as uroglaucin and cyanourine, have in most cases really been indigo, and possibly have been so in all: it is, at least,

* Braconnot, Journal de Chemie Médicale, tom. i. p. 454.

† Arch. f. Chem. u. Mikrosk., bd. 2. s. 161, 173.

singular that I should so frequently have met with indigo in urine, the occurrence of which has hitherto been deemed so rare, and not have fallen in with a single case of cyanourine or uroglaucin, the presence of which might be considered, from the inquiries of BRACONNOT, SCHERER and HELLER, to be so much more common.

Taking into consideration then the whole of the facts and observations recorded in this communication, the following conclusions remain to be deduced :—

1st. That blue indigo is frequently formed in human urine; the quantity being subject to the greatest variation. In some cases it is so considerable as to impart a deep green or bluish-green colour to the whole urine, and to form a pellicle of nearly pure indigo over the whole surface of the liquid. In others the blue scum is formed, but the urine itself does not become either blue or green; and occasionally the quantity is so small, that it can only be detected by means of the microscope.

2nd. That for the formation of this indigo, it is in general necessary that the urine should be exposed to the air for some days in an open vessel, when oxygen is absorbed and the blue indigo developed. Whatever facilitates therefore oxygenation, as free exposure to light, air, and warmth, hastens the development of the blue indigo; hence in summer the changes described take place much more quickly than in winter. On the contrary, these changes are retarded, and even altogether prevented, by a more or less complete exclusion of oxygen. By this exclusion, blue indigo is deprived of its colour; and it may be reduced or reformed, alternately, according as air or oxygen is excluded or admitted to urine containing it. From one or two cases elsewhere recorded, however, it would appear that blue indigo is occasionally formed in the system, and is voided as such in the urine.

3rd. That there is usually, but not always, found with the blue indigo, where the amount of this is very considerable, a brown extractive, sometimes in large quantity, which closely resembles hæmatin in its chemical manifestations and elementary composition; the aqueous solution of this, when exposed to the air, yields a further supply of coloured indigo.

4th. That the urines in which the coloured indigo occurs in the largest quantities are usually of a pale straw-colour, readily becoming turbid; they are alkaline, and of rather low specific gravity. Small quantities of indigo are, however, frequently found in urines possessing characters the very reverse, that is, in such as are high coloured and of high specific gravity; but as a rule, the blue pigment is usually absent from these urines, and in only a few cases is it formed in them in any considerable amount.

5th. That between hæmatin, urine-pigment, and indigo very close chemical and physiological relations exist, rendering it highly probable that the indigo formed in the urine is in many cases immediately derived from altered or modified hæmatin or urine-pigment. Urine-pigment is itself usually regarded as but a modification of hæmatin.

6th. That the chemical composition of indigo would lead to the inference that when that substance is present in large quantities in the urine, it forms a vehicle for

the elimination of excess of carbon from the system; this view is confirmed by the nature of the cases in which indigo has been met with in the largest quantities in human urine, namely in cases of phthisis involving extensive pulmonary disease, and in cholera.

7th. There appears strong reason for believing that the blue pigments, cyanourine and uroglaucin, if not identical with, are but states or modifications of indigo, since they resemble that substance in many of their chemical and physiological relations, and in their ultimate composition.

XIV. *On certain Properties of square numbers and other quadratic forms, with a Table of odd numbers from* 1 *to* 191, *divided into* 4, 3 *or* 2 *square numbers, the algebraic sum of whose roots (positive or negative) may equal* 1, *by means of which Table all the odd numbers up to* 9503 *may be resolved into not exceeding* 4 *square numbers. By Sir* Frederick Pollock, *F.R.S., Lord Chief Baron.*

Received, Dec. 20, 1853,—Read, Dec. 22, 1853,—Revised by the Author, Nov. 1854.

SOME years ago, in examining the properties of the triangular or trigonal numbers

$$0, 1, 3, 6, 10, 15, \&c. \quad \frac{n.(n-1)}{2},$$

I observed that every trigonal number was composed of 4 trigonal numbers, viz. 3 times some prior trigonal number plus the next in the series, either immediately before or after that prior number;

thus
$$45=10+10+10+15$$
$$55=15+15+15+10;$$

or generally, as all numbers are of the form $2n-1$ or of $2n$, all trigonal numbers are of one of the 2 forms, $2n^2-n$, $2n^2+n$,

$$2n^2-n=\frac{n^2-n}{2}\times 3+\frac{n^2+n}{2}$$

and

$$2n^2+n=\frac{n^2+n}{2}\times 3+\frac{n^2-n}{2}.$$

I found also that all the natural numbers in the interval between any two consecutive trigonal numbers, might be composed of 4 trigonal numbers, having the sum of their bases or roots *constant*, viz. the sum of the roots or bases of the 4 trigonal numbers which compose the first of the 2 trigonal numbers.

This will be best explained by an example: the roots or bases are placed over the numbers, and it will be observed their sum is constant in the same interval.

$\frac{8\times9}{2}=$ **36**	**3 6**	**4 10**	**4 10**	**4 10**	=15
37	3 6	3 6	4 10	5 15	15
38	2 3	4 10	4 10	5 15	15
39	2 3	3 6	5 15	5 15	15
40	2 3	3 6	4 10	6 21	15
41	1 1	4 10	5 15	5 15	15
42	1 1	4 10	4 10	6 21	15
43	1 1	3 6	5 15	6 21	15
44	2 3	2 3	4 10	7 28	15
$\frac{9\times10}{2}=$ **45**	**4 10**	**4 10**	**4 10**	**5 15**	17
46	3 6	4 10	5 15	5 15	17
47	3 6	4 10	4 10	6 21	17
48	3 6	3 6	5 15	6 21	17
49	2 3	4 10	5 15	6 21	17
50	3 6	3 6	4 10	7 28	17
51	2 3	4 10	4 10	7 28	17
52	2 3	3 6	5 15	7 28	17
53	1 1	4 10	6 21	6 21	17
54	1 1	4 10	5 15	7 28	17
$\frac{10\times11}{2}=$ **55**	**4 10**	**5 15**	**5 15**	**5 15**	=19

From 55 to 66 ($=^{5}15, ^{5}15, ^{5}15, ^{6}21$) the constant sum of the bases will be 19, and this may be continued without limit.

If the law by which this can be continued were discovered and proved, it would furnish the means of proving FERMAT's theorems of the polygonal numbers; but not being aware of any law by which the series that fills up the intervals could be continued, I turned my attention to the square numbers as containing (apparently) a greater variety of theorems, and as being (certainly) of all quadratic forms that which

is most familiar, and in which calculations or comparisons may be made with the greatest facility.

Very lately I observed the following property of square numbers:—

If any four square numbers a^2, b^2, c^2, d^2 have their roots such that by making one or more positive and the rest negative, the algebraic sum of the roots may equal 1; then if the roots whose sum is one less than the others be each increased by 1, and the others be each decreased by 1, the sum of the squares of the roots thus increased and decreased will be equal to $a^2+b^2+c^2+d^2+2$. Let $a+b-c-d=1$, and let c and d become $c+1$, $d+1$, and let a and b become $a-1$, $b-1$, then

$$(a-1)^2+(b-1)^2+(c+1)^2+(d+1)^2=a^2+b^2+c^2+d^2+2\times(-a-b+c+d)+4,$$

but

$$2\times(-a-b+c+d)=-2,$$

therefore the sum of the squares of the new roots$=a^2+b^2+c^2+d^2+2$. If $a-b-c-d=1$, the result is the same, decreasing a and increasing each of b, c and d by 1.

The theorem is more general (as might have been expected).

Theorem A.

For if instead of 1 the algebraic sum of the roots be equal to $2n-1$, and the negative roots be numerically increased by n and the positive roots be decreased by n, the increase in the sum of the squares of the new roots thus formed will be $2n$.

Let $a+b-c-d=2n-1$, then $(a-n)^2+(b-n)^2+(c+n)^2+(d+n)^2=a^2+b^2+c^2+d^2-2an-2bn+2cn+2dn+4n^2$, but $-2an-2bn+2cn+2dn=-(2n-1)\times 2n=-4n^2+2n$, $\therefore$ the sum of the squares of the new roots$=a^2+b^2+c^2+d^2+2n$.

The following table shows the result of different algebraic sums of the roots, with the corresponding increase or decrease of roots and increase of the sum of the squares.

Sum of roots.	Corresponding increase or decrease of roots.	Increase of sum of squares.
1	1	2
3	2	4
5	3	6
7	4	8
9	5	10
11	6	12
&c.	&c.	&c.

There is a similar theorem with respect to the decrease of the sum of the squares.

Theorem B.

If $a+b-c-d=2n+1$ (instead of $2n-1$), then if a and b be each diminished and c and d be increased by n, the sum of the squares of the new roots will be less by $2n$, and $(a-n)^2+(b-n)^2+(c+n)^2+(d+n)^2$ will equal $a^2+b^2+c^2+d^2-2n$.

And a similar table will show the corresponding decrease of the sum of the squares.

Sum of roots.	Increase and decrease.	Decrease of sum of squares.
3	1	2
5	2	4
7	3	6
9	4	8
&c.	&c.	&c.

The use that may be made of these theorems will best appear by an example or two.

51 is composed of 4 square numbers, 25, 16, 9, 1, whose roots are 5, 4, 3, 1.

$$4 + 3 - 5 - 1 = 1$$
$$5 + 3 - 4 - 1 = 3$$
$$5 + 4 - 3 - 1 = 5$$
$$5 + 4 + 1 - 3 = 7$$

Then by Theorem A. square numbers which compose 53, 55, 57, and 59 may be obtained, and by Theorem B. those which compose 49, 47, and 45 by adding to or subtracting from the roots; thus

$5 + 4 - 3 - 1 = 5 = 2 \times 3 - 1, n = 3$

3 3 3 3 being deducted or added,

2 1 6 4 become the new roots, the sum of whose squares $= 57 = 51 + 2 \times 3$.

$5 + 4 + 1 - 3 = 7 = 2 \times 3 + 1, n = 3$

3 3 3 3

2 1 − 2 6 are the new roots, the sum of whose squares $= 45 = 51 - 2 \times 3$.

Again, 5 5 1 0 are roots of squares which compose 51,

$5 + 5 + 1 \quad 0 = 11 = 2 \times 6 - 1, n = 6$

6 6 6 6

1 1 − 5 6 the squares of these new roots $= 63 = 51 + 12\ (51 + 2 \times 6)$. Also,

$5 + 5 - 1 \quad 0 = 9 = 2 \times 5 - 1, n = 5$

5 5 5 5

0 0 6 5 the squares of these new roots = 61 by Theorem A.; by Theorem B. the squares which compose 41 and 43 may be found, and thus the square numbers (not exceeding 4) which compose 51 being given, square numbers not exceeding 4 may be discovered, which compose 41, 43, and all the intermediate odd numbers up to 63.

This method of obtaining the square numbers that compose a succession of odd numbers, suggested that if a method similar to what was observed in the trigonal numbers were adopted as to the square numbers, the series of odd numbers might be

resolved into square numbers. In the trigonal numbers the successive bases of the 4 trigonal numbers into which the terms of the trigonal series are each divisible, are

0	0	0	1
0	1	1	1
1	1	1	2
1	2	2	2
2	2	2	3
2	3	3	3 &c.

If instead of using these numbers as bases or roots of trigonal numbers they be squared and added together, they furnish a series (1, 3, 7, 13, 21, 31, &c.) whose general term is m^2+m+1, or according as m is even or odd, $4n^2\pm 2n+1$: this expression is manifestly divisible into square numbers whose roots will be either $n, n, n, n+1$ or $n-1, n, n, n$, and the sum of the roots will be $4n\pm 1$, and with reference to integral quantities will be a maximum. The terms of the series 1, 3, 7, 13, &c., furnish steps, places, or positions at which the process of increasing the sum of the squares might commence again, and as far as any law of increase is applicable to one term it is applicable to all. I have therefore called this series 1, 3, 7, 13, &c. the gradation-series of this system of resolving the odd numbers into square numbers not exceeding 4.

I have prepared a table in which the odd numbers from 1 to 191, respectively, are divided into square numbers not exceeding 4, the algebraic sum of whose roots may be made equal to 1.

This table of the odd numbers up to 191 is at the end of the paper; the terms of the gradation-series (as they occur) are distinctively denoted, and all the sets of roots of the odd numbers up to 191 are capable of forming 1 as their algebraic sum; and by means of this series any odd number from $4n^2\pm 2n+1$ up to $4n^2\pm 2n+191$ inclusive, may be divided into not exceeding 4 square numbers, whatever be the value of n.

The examination of this series led me to observe a remarkable property of odd numbers with reference to the square numbers (not exceeding 4) into which they may be divided, and which may be stated in the following theorem.

Theorem C.

Every odd number may be divided into square numbers (not exceeding 4), the algebraic sum of whose roots (positive or negative) will (in some form of the roots) be equal to every odd number from 1 to the greatest possible sum of the roots, or the theorem may be stated in a purely algebraical form thus:

If there be 2 equations,

$$a^2+b^2+c^2+d^2=2n+1$$

and

$$a+b+c+d=2r+1,$$

a, b, c, d being each integral or nil, n and r being positive, and r a maximum, then if

any positive integer r' (not greater than r) be assumed, it will always be possible to satisfy the pair of equations

$$w^3=x^3+y^3+z^3=2n+1$$
$$w+x+y+z=2r'+1$$

by integral values (positive, negative, or nil) of w, x, y, z.

I now propose to show in what manner the table may be used, so as to divide into square numbers (not exceeding 4) any odd number from 1 up to 9503, and any odd number whatever of the form $4n^2\pm 2n+2p+1$, where p is not greater than 95 [$95\times 2+1=191$].

If $2p+1=a^2+b^2+c^2+d^2$, and if also $a+b+c+d=1$ (a, b, c, d being integral numbers, positive, negative or nil), in other words, if the odd number $2p+1$ be such that the algebraic sum of the roots of the square numbers (not exceeding 4) which compose it may be equal to 1, then it will follow that $m^2+m+1+2p$ may be resolved into square numbers (not exceeding 4) the sum of whose roots will equal $2m+1$, for m^2+m+1 is of the form $4n^2\pm 2n+1$; let it equal it, and $m^2+m+1+2p=4n^2\pm 2n$, $(a+b+c+d)+a^2+b^2+c^2+d^2=(n\pm a)^2+(n\pm b)^2+(n\pm c)^2+(n\pm d)^2$ (manifestly 4 square numbers), and the sum of the roots$=4n\pm(a+b+c+d)=4n\pm 1=2m+1$.

Let the function m^2+m+1 be designated by the notation fm. If every odd number from 1 up to $2m+1$ can be resolved into (not exceeding) 4 square numbers, the algebraic sum of whose roots may equal 1, then every odd number from fm to $fm+2m$ inclusive may be resolved into 4 square numbers, the sum of whose roots may equal $2m+1$; but the next odd number to $fm+2m$ is $f(m+1)$, and since $f(m+1)$ is resolvable into 4 square numbers, the sum of whose roots$=2m+3$; if every odd number from 1 up to $2m+1$ can be resolved into not exceeding 4 square numbers the algebraic sum of whose roots$=1$, then every odd number from 1 up to $f(m+1)+2m$ is resolvable into 4 square numbers, and $f(m+1)+2m=m^2+5m+3$.

In the Table the highest odd number $191=2\times 95+1$, therefore $m=95$; and every odd number from 1 up to $95^2+5\times 95+3=9503$ may be resolved into not exceeding 4 square numbers, by means of the Table, also every odd number of the form $4n^2\pm 2n+2p+1$, whatever be the value of n, provided p be not greater than 95; for example, let it be required to resolve 9301 into 4 square numbers, the next less number of the form m^2+m+1 is $9121=95^2+95+1=4\cdot 48^2-2\cdot 48+1$, $9301=9120+181$.

181 by the Table is resolvable into

$$1^2+4^2+8^2+10^2$$

and $-1+4+8-10=1$ $9301=(48+1)^2+(48-4)^2+(48-8)^2+(48+10)^2$

$$=49^2+44^2+40^2+58^2;$$

so $4n^2\pm n+181$ is always resolvable into 4 square numbers, whatever be the value of n, and the roots of the square numbers will be $(n\mp 1)$, $(n\pm 4)$, $(n\pm 8)$, $(n\mp 10)$.

If the following series of equations be assumed,

$$1+2d=2q+1$$
$$3+2d_1=2q+1$$
$$7+2d_2=2q+1$$
$$13+2d_3=2q+1$$
$$m^2+m+1+2d_{m-1}=2q+1,$$

and if each of the quantities $2d+1, 2d_1+1, 2d_2+1, 2d_3+1 \ldots 2d_{m-1}+1$ can be resolved into 4 square numbers, the algebraic sum of whose roots$=1$, then the given odd number $2q+1$ may be resolved into successive sets of 4 squares, the sum of whose roots will be successively 1, 3, 5, 7 ... $2m+1$. Hence an odd number, $2q+1$, may be resolved into 4 square numbers, the sum of whose roots shall be equal to $2p+1$, if upon adding 1 to the difference between $2q+1$ and the $(p+1)^{th}$ term of the gradation-series, the difference so increased can be resolved into 4 square numbers, the algebraic sum of whose roots$=1$. If it be required to resolve 37 into 4 squares, the sum of whose roots shall equal $7=2\times3+1$, here $p=3$, the $(p+1)^{th}$ or 4th term of the gradation-series is 13; 13 is of the form $4\cdot2^2-2\cdot2+1$, and it equals $2^2+2^2+2^2+1^2$ $(2-1)^2$; the difference between 37 and $14=24$, increased by $1=25$, $25=1^2+2^2+2^2$ $+4^2$, and the roots $+1-2-2+4=1$ and $13+24=(2+2)^2=4^2, 4^2, 1^2, -2^2$

$$(2+2)^2$$
$$(2-1)^2$$
$$(2-4)^2$$

and $+4+4+1-2=7$.

If, therefore, every odd number can be resolved into integral square numbers (not exceeding 4) whose algebraic sum will equal 1, then every odd number can be resolved into integral square numbers (not exceeding 4) whose algebraic sum will be 1, 3, 5, &c. [viz. *all the odd numbers up to the maximum*].

I propose (in order not to leave the Theorem C. unproved) to show by the properties of numbers already proved, that every odd number may be resolved into integral square numbers (not exceeding 4) whose algebraic sum will equal 1.

Every odd number may be represented by $2p+1$ (p being any integer): then by FERMAT'S theorem of the polygonal numbers (as proved by LEGENDRE, Théorie des nombres), p must either be a trigonal number, or composed of two or three trigonal numbers. If it be a trigonal number, then $p=\frac{q^2+q}{2}$, and $2p+1=q^2+q+1$, which equals $4n^2\pm2n+1$, which is divisible into $(n\pm1)^2, n^2, n^2, n^2$, and $n-n\mp n.\pm(n\pm1)=1$.

If p be composed of 2 trigonal numbers, $p=\frac{q^2+q}{2}+\frac{r^2+r}{2}$, and the sum of any two trigonal numbers is of the form of a^2+a+b^2* and may be assumed equal to a^2+a+b^2,

* If 2 numbers be both odd or both even, they may always be represented by $a+b$ and $a-b$; if one be odd and the other even, they may always be represented by $a+b\pm1$, $a-b$ or $a+b$, $a-b\pm1$; and if the 2 numbers be made the bases of trigonal numbers, the sum of the 2 trigonal numbers will always be of the form a^2+a+b^2 or a^2+b+b^2.

therefore $2p+1=2a^2+2a+2b^2+1=(a+1)^2$, a^2, b^2, b^2, and the roots $(a+1)$, $-a$, b, $-b$, $=1$. If p be composed of 3 trigonal numbers, then $p=a^2+a+b^2+\frac{m^2+m}{2}$ and $2p+1=2a^2+2a+2b^2+m^2+m+1$, but m^2+m+1 is of the form $4n^2\pm 2n+1$, whose four roots (as already seen) are $n\pm 1$, n, n, n, and if these roots be varied thus,

$$\begin{array}{c} \mp a+n\pm 1 \\ a-n \\ b+n \\ b-n, \end{array}$$

the squares of these four roots will equal $2a^2+2a+2b^2+4n^2\pm 2n+1$, and the algebraic sum of these roots obviously may $=1$. It follows from this, that every possible odd number may be divided into integral square numbers (not exceeding 4), the algebraic sum of whose roots $=1$.

I propose in a future communication to give a different proof of the Theorem C, and instead of proving the Theorem C. by FERMAT'S proposition of the trigonal numbers, I shall offer a proof of FERMAT'S proposition of the trigonal numbers by the Theorem C; it is obvious that they are so connected that either may be proved from the other.

I am not aware that the theorems A, B, or C, or the method above described of using a gradation-series, have ever been noticed before, and as they appear to add something (however little) to the theory of numbers, I have ventured to present them to the attention of the Royal Society.

NOTE.—Numbers of the form $2n+2$ (*even numbers*) may be resolved into square numbers (not exceeding 4), the algebraic sum of whose roots may always equal 2, and so far they have an analogous property, but they do not possess the analogous property of being resolvable into roots whose algebraic sum will $=2, 4, 6, 8,$ &c.

TABLE of odd numbers and of the Roots of the squares (not exceeding 4) into which they may be divided, whose algebraic sum may equal 1.

Odd numbers.	Roots of the Squares into which they may be divided whose algebraic sum may equal 1.	Odd numbers.	Roots of the Squares into which they may be divided whose algebraic sum may equal 1.	Odd numbers.	Roots of the Squares into which they may be divided whose algebraic sum may equal 1.
1	**0 0 0 1**	65	2 3 4 6	129	2 5 6 8
3	**0 1 1 1**	67	1 1 4 7	131	0 5 5 9
5	0 0 1 2	69	1 4 4 6	**133**	**5 6 6 6**
7	**1 1 1 2**	71	1 3 5 6	135	5 5 6 7
9	0 1 2 2	**73**	**4 4 4 5**	137	4 6 6 7
11	0 1 1 3	75	3 4 5 5	139	4 5 7 7
13	**1 2 2 2**	77	3 4 4 6	141	4 5 6 8
15	1 1 2 3	79	3 3 5 6	143	2 3 7 9
17	0 2 2 3	81	2 4 5 6	145	3 6 6 8
19	0 1 3 3	83	0 3 5 7	147	3 5 7 8
21	**2 2 2 3**	85	2 4 4 7	149	2 3 6 10
23	1 2 3 3	87	2 3 5 7	151	3 5 6 9
25	1 2 2 4	89	0 2 6 7	153	2 2 8 9
27	1 1 3 4	**91**	**4 5 5 5**	155	3 4 7 9
29	0 2 3 4	93	4 4 5 6	**157**	**6 6 6 7**
31	**2 3 3 3**	95	3 5 5 6	159	5 6 7 7
33	2 2 3 4	97	3 4 6 6	161	5 6 6 8
35	1 3 3 4	99	3 4 5 7	163	5 5 7 8
37	1 2 4 4	101	0 1 6 8	165	4 6 7 8
39	1 2 3 5	103	2 5 5 7	167	1 2 9 9
41	0 0 4 5	105	2 4 6 7	169	4 6 6 9
43	**3 3 3 4**	107	1 3 4 9	171	4 5 7 9
45	2 3 4 4	109	2 4 5 8	173	1 6 6 10
47	2 3 3 5	**111**	**5 5 5 6**	175	3 6 7 9
49	2 2 4 5	113	4 5 6 6	177	4 5 6 10
51	1 3 4 5	115	4 5 5 7	179	3 5 8 9
53	2 2 3 6	117	4 4 6 7	181	1 4 8 10
55	1 3 3 6	119	3 5 6 7	**183**	**6 7 7 7**
57	**3 4 4 4**	121	2 2 7 8	185	6 6 7 8
59	3 3 4 5	123	3 5 5 8	187	5 7 7 8
61	2 4 4 5	125	3 4 6 8	189	5 6 8 8
63	2 3 5 5	127	1 3 6 9	191	5 6 7 9

XV. *On the Thermal Effects of Fluids in Motion.*—Part II.

By J. P. Joule, *F.R.S.* and Professor W. Thomson, *M.A.*, *F.R.S.*

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In the last experiment related in our former paper*, in which a low pressure of air was employed, a considerable variation of the cooling effect was observed, which it was necessary to account for in order to ascertain its influence on the results. We therefore continued the experiments at low pressures, trying the various arrangements which might be supposed to exercise influence over the phenomena. We had already interposed a plug of cotton wool between the iron and copper pipes, which was found to have the very important effect of equalizing the pressure, besides stopping any solid or liquid particles driven from the pump, and which has therefore been retained in all the subsequent experiments. Another improvement was now effected by introducing a nozle constructed of boxwood, instead of the brass one previously used. This nozle is represented by fig. 1. Plate IV., in which *a a* is a brass casting which bolts upon the terminal flange of the copper piping, *b b* is a turned piece of boxwood screwing into the above, having two ledges for the reception of perforated brass plates, the upper plate being secured in its place by the turned boxwood *c c*, which is screwed into the top of the first piece. The space enclosed by the perforated plates is 2·72 inches long and an inch and a half in diameter, and being filled with cotton, silk, or other material more or less compressed, presents as much resistance to the passage of the air as may be desired. A tin can *d*, filled with cotton wool, and screwing to the brass casting, serves to keep the water of the bath from coming in contact with the boxwood nozle.

In the following experiments, made in order to ascertain the variations in the cooling effect above referred to, the nozle was filled with 382 grs. of cotton wool, which was sufficient to keep up a pressure of about 34 lbs. on the inch in the tubes, when the pump was working at the ordinary rate. By opening the stopcock in the main pipe this pressure could be further reduced to about 22 lbs. by diminishing the quantity of air arriving at the nozle. By shutting and opening the stopcock we had therefore the means of producing a temporary variation of pressure, and of investigating its effect on the temperature of the air issuing from the nozle. In the first experiments the stopcock was kept open for a length of time, until the temperature of the rushing air became pretty constant; it was then shut for a period of $3\frac{3}{4}$, $7\frac{1}{2}$, 15, 30 or 60 seconds, then reopened. The oscillations of temperature thus pro-

* Philosophical Transactions (June), 1853, Part III.

duced are laid down upon the Chart No. 1, in which the ordinates of the curves represent the temperatures according to the scale of thermometer C, each division corresponding to 0·0477 of a degree Centigrade. The divisions of the horizontal lines represent intervals of time equal to a quarter of a minute. The horizontal black lines show the temperature of the bath in each experiment.

The effect upon the pressure of the air produced by shutting the stopcock during various intervals of time, is given in the following Table:—

Stopcock shut for	5ˢ.	15ˢ.	30ˢ.	1ᵐ.	2ᵐ.
m s					
Initial pressure.....	22·35	22·35	22·35	22·35	22·35
Pressure after..... 0 5	24·92	24·92	24·92	24·92	24·92
Pressure after..... 0 15	23·07	28·46	28·46	28·46	28·46
Pressure after..... 0 30	22·43	23·38	30·84	30·84	30·84
Pressure after..... 0 45	22·35	22·5	24·27	32·03	32·03
Pressure after..... 1 0	22·35	22·43	22·83	32·79	32·79
Pressure after..... 1 15	.....	22·35	22·45	24·54	33·08
Pressure after..... 1 30	.....	22·35	22·35	22·83	33·25
Pressure after..... 1 45	.....	.....	22·35	22·43	33·33
Pressure after..... 2 0	.....	.....	.....	22·35	33·41
Pressure after..... 2 15	.....	.....	.....	22·35	24·54
Pressure after..... 2 30	.....	.....	.....	.....	22·54
Pressure after..... 2 45	.....	.....	.....	.....	22·40
Pressure after..... 3 0	.....	.....	.....	.....	22·35

The last column gives also the effect occasioned by the permanent shutting or opening of the stopcock, 33·41 lbs. being nearly equal to the pressure when the stopcock has been closed for a long time.

In the next experiments, the opposite effect of opening the stopcock was tried, the results of which are laid down on Chart No. 2.

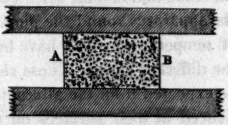
The effect upon the pressure of the air produced by opening the stopcock during the various intervals of time employed in the experiments, is exhibited in the next Table:—

Stopcock opened for	3¾ˢ.	7½ˢ.	15ˢ.	30ˢ.	1ᵐ.
m s					
Initial pressure	34·37	34·37	34·37	34·37	34·37
Pressure after..... 0 3¾	29·57	29·57	29·57	29·57	29·57
Pressure after..... 0 7½	.....	27·43	27·43	27·43	27·43
Pressure after..... 0 15	32·47	30·41	25·15	25·15	25·15
Pressure after..... 0 30	33·5	32·47	30·41	23·23	23·23
Pressure after..... 0 45	33·94	33·5	32·4	29·4	22·9
Pressure after..... 1 0	34·1	34·1	33·5	32·13	22·76
Pressure after..... 1 15	34·2	34·3	33·94	33·24	28·82
Pressure after..... 1 30	34·33	34·37	34·14	33·90	31·44
Pressure after..... 1 45	34·37	34·37	34·30	34·14	32·9
Pressure after..... 2 0	.....	.....	34·37	34·33	33·66
Pressure after..... 2 15	.....	.....	.....	34·37	34·06
Pressure after..... 2 30	.....	.....	.....	.....	34·20
Pressure after..... 2 45	.....	.....	.....	.....	34·37

The remarkable fluctuations of temperature in the issuing stream accompanying such changes of pressure, and continuing to be very perceptible in the different cases

for periods of from 3 or 4 minutes up to nearly half an hour after the pressure had become sensibly uniform, depend on a complication of circumstances, which appear to consist of (1) the change of cooling effect due to the instantaneous change of pressure; (2) a heating or cooling effect produced instantaneously by compression or expansion in all the air flowing towards and entering the plug, and conveyed through the plug to the issuing stream; and (3) heat or cold communicated by contact from the air on the high-pressure side, to the metals and boxwood, and conducted through them to the issuing stream.

The first of these causes may be expected to influence the issuing stream instantaneously on any change in the stopcock; and after fluctuations from other sources have ceased, it must leave a permanent effect in those cases in which the stopcock is permanently changed. But after a certain interval the reverse agency of the second cause, much more considerable in amount, will begin to affect the issuing stream, will soon preponderate over the first, and (always on the supposition that this convection is uninfluenced by conduction of any of the materials) will affect it with all the variations, undiminished in amount, which the air entering the plug experiences, but behind time by a constant interval equal to the time occupied by as much air as is equal in thermal capacity to the cotton of the plug, in passing through the apparatus*; this, in the experiments with the stopcock shut, would be very exactly a



* To prove this, we have only to investigate the convection of heat through a prismatic solid of porous material, when a fluid entering it with a varying temperature is forced through it in a continuous and uniform stream. Let A B be the porous body, of length a and transverse section S; and let a fluid be pressed continuously through it in the direction from A to B, the temperature of this fluid as it enters at A being an arbitrary function F (t) of the time. Then if v be the common temperature of the porous body and fluid passing through it, at a distance x from the end A, we have

$$\sigma\frac{dv}{dt}=k\frac{d^2v}{dx^2}-\frac{\theta}{S}\frac{dv}{dx}; \quad \ldots\ldots\ldots\ldots\ldots (1)$$

if k be the conducting power of the porous solid for heat (the solid surrounding it being supposed to be an infinitely bad conductor, or the circumstances to be otherwise arranged, as is practicable in a variety of ways, so that there may be no lateral conduction of heat), σ the thermal capacity of unity of its bulk, and θ the thermal capacity of as much of the fluid as passes in the unit time. Now if, as is probably the case in the actual circumstances, conduction through the porous solid itself is insensible in its influence as compared with the convection of the fluid, this equation will become approximately

$$\sigma\frac{dv}{dt}=-\frac{\theta}{S}\frac{dv}{dx}, \quad \ldots\ldots\ldots\ldots\ldots (2)$$

which, in fact, expresses rigorously the effect of the second cause mentioned in the text if alone operative.

If F denote any arbitrary function, and if θ be supposed to be constant, the general integral of this equation is—

$$v=F\left(t-\frac{\sigma S}{\theta}x\right); \quad \ldots\ldots\ldots\ldots\ldots (3)$$

and if the arbitrary function be chosen to express by F (t) the given variation of temperature where the fluid enters the porous body, we have the particular solution of the proposed problem. We infer from it that, at any distance x in the porous body from the entrance, the temperature will follow the same law and extent of

quarter of a minute; but it appears to have averaged more nearly one-third of a minute in the varying circumstances of the actual experiments, since our observations (as may be partially judged from the preceding charts) showed us with very remarkable sharpness, in each case about twenty seconds after the shutting or opening of the stopcock, the commencement of the heating or cooling effect on the issuing stream, due to the sudden compression or rarefaction instantaneously produced in the air on the other side of the plug.

The entering air will, very soon after its pressure ceases to vary, be reduced to the temperature of the bath by the excellent conducting action of the spiral copper pipe through which it passes; and, consequently, twenty seconds or so later, the issuing stream can experience no further fluctuations in temperature except by the agency depending on the third cause.

That the third cause may produce very considerable effects is obvious, when we think how great the variations of temperature must be to which the surfaces of the solid materials in the neighbourhood of the plug on the high-pressure side are subjected during the sudden changes of pressure: and that the heat consequently taken in or emitted by these bodies may influence the issuing stream perceptibly for a quarter or a half hour after the changes of pressure from which it originated have ceased, is quite intelligible on account of the slowness of conduction of heat through the wood and metals, when we take into account the actual dimensions of the parts of the apparatus round the plug. It is not easy, however, to explain all the fluctuations of temperature which have been observed after the pressure had become constant in the different cases. Those shown in the first set of diagrams are just such as might be expected from the alternate heating and cooling which the solids must have experienced at their surfaces on the high-pressure side, and which must be conducted through so as to affect the issuing stream after a considerable time; but the great

variation as at the entrance, only later in time by an interval equal to $\frac{\sigma S}{\theta} x$. We conclude that the variations of temperature in the issuing stream due to the second cause alone, in the actual circumstances, are equal and similar to those of the air entering the plug, but later in time by $\frac{\sigma S a}{\theta}$. In this expression, the numerator, $\sigma S a$, denotes simply the thermal capacity of the whole plug. The plug, in the actual experiments, having consisted of 382 grains of cotton, of which the thermal capacity is about 191 times that of a grain of water, and (when the stopcock was closed) the air having been pumped through at the rate, per second, of 50 grains, of which the capacity is twelve times that of a grain of water, the value of $\frac{\sigma S a}{\theta}$ must have been $\frac{191}{12}$ seconds, or about a quarter of a minute. When the stopcock was open, an unknown quantity of air escaped through it, and therefore the value of $\frac{\sigma S a}{\theta}$ must have been somewhat greater. The variation which the value of θ must have experienced when the stopcock was opened or closed in the course of an experiment, or even merely in consequence of the change of pressure following the initial opening or closing of the stopcock, makes the circumstances not such as in any of the cases to correspond rigorously to the preceding solution; which, notwithstanding, represents the general nature of the convective effect nearly enough for the explanation in the text.

elevations of temperature shown in the second set of diagrams, which correspond to cases when the pressure was temporarily or permanently *diminished*, are not, so far as we see, explained by the causes we have mentioned, and the circumstances of these cases require further examination.

When we had thus examined the causes of the fluctuations of temperature in the issuing air, the precautions to prevent their injurious effect upon the accuracy of the determinations of the cooling effect in the passage of air through the porous plug became evident. These were simply to render the action of the pump as uniform as possible, and to commence the record of observations only after one hour and a half or two hours had elapsed from the starting of the pump. The system then adopted was to observe the thermometers in the bath and stream of air, and the pressure-gauge every two minutes or minute and a half; the means of which observations are recorded in the columns of the Tables. In some instances the air previous to passing into the pump was transmitted through a cylinder which had been filled with quicklime. But since by previous use its power of absorbing water had been considerably deteriorated, a portion of the air was always transmitted through a LIEBIG tube containing asbestos moistened with sulphuric acid or chloride of zinc. The influence of a small quantity of moisture in the air is trifling, but will hereafter be examined. That of the carbonic acid contained by the atmosphere was, as will appear in the sequel, quite inappreciable. It will be proper to observe that the thermometers by which the temperature of the bath and issuing air was ascertained, were repeatedly compared together to avoid any error which might arise from the alteration of their fixed points from time to time.

TABLE I.—Experiments with a plug consisting of 191 grains of cotton wool.

1.	2.	3.	4.	5.	6.	7.	8.
Number of observations from which the results in Columns 4, 6, and 7, are obtained.	Cubic inches passed through the nozle per minute.	Water in 100 grains of air, in grains.	Pressure in lbs. on the square inch.	Atmospheric pressure.	Temperature of the bath.	Temperature of the issuing air.	Cooling effect in Cent. degrees.
20	10822	0·51	21·326	14·400	20°·295	20°·201	0°·094
20	10998	0·30	21·239	14·252	16·740	16·615	0·125
10	Not observed.	0·56	20·446	14·609	17·738	17·622	0·116
10	10769	0·66	20·910	14·772	16·039	15·924	0·115
10	10769	0·66	20·934	14·775	16·065	15·967	0·098
10	10769	0·66	20·995	14·779	16·084	15·984	0·100
10	10769	0·66	20·933	14·782	16·081	15·974	0·107
Mean	.....	0·57	20·969	14·624	17·006	16·898	0·108

In each, excepting the first of the seven experiments above recorded, the air was passed through the quicklime cylinder.

In the next experiments the nozle was filled with 382 grains of cotton wool. The

intermediate stopcock was however partly opened, in order that by discharging a portion of the air before its arrival at the nozle, the pressure might not be widely different from that employed in the last series. In all excepting the last experiment recorded in the following Table, the cylinder of lime was dispensed with.

TABLE II.—Experiments with a smaller quantity of air passed through a plug consisting of 382 grs. of cotton wool.

1.	2.	3.	4.	5.	6.	7.	8.
Number of observations from which the results in Columns 4, 6, and 7, are obtained.	Cubic inches passed through the nozle per minute.	Water in 100 grains of air, in grains.	Pressure in lbs. on the square inch.	Atmospheric pressure.	Temperature of the bath.	Temperature of the issuing air.	Cooling effect in Cent. degrees.
20	3865	0·59	22·614	14·513	20°·363	20°·224	0°·139
30	3960	0·73	22·818	14·514	19·853	19·769	0·084
20	Not observed.	0·56	22·818	14·604	20·481	20·407	0·074
45	3125	0·65	22·296	14·590	20·584	20·313	0·271
20	Not observed.	1·23	23·000	14·518	18·636	18·476	0·160
36	Not observed.	1·20	22·616	14·520	20·474	20·336	0·138
50	Not observed.	1·36	22·582	14·518	20·485	20·325	0·160
Mean	.....	0·90	22·678	14·540	20·125	19·979	0·146

TABLE III.—Experiments in which the entire quantity of air propelled by the pump was passed through a plug consisting of 382 grains of cotton wool. The cylinder of lime was not employed.

1.	2.	3.	4.	5.	6.	7.	8.
Number of observations from which the results in Columns 4, 6, and 7, are obtained.	Cubic inches passed through the nozle per minute.	Water in 100 grains of air, in grains.	Pressure in lbs. on the square inch.	Atmospheric pressure.	Temperature of the bath.	Temperature of the issuing air.	Cooling effect in Cent. degrees.
7	11766	0·56	36·625	14·583	19°·869	19°·535	0°·334
10	Not observed.	0·56	35·671	14·790	20·419	20·098	0·321
10	Not observed.	0·36	35·772	14·504	16·096	15·730	0·366
10	Not observed.	0·36	35·872	14·504	16·104	15·721	0·383
10	Not observed.	0·36	36·026	14·504	16·232	15·869	0·363
Mean	.....	0·44	35·993	14·577	17·744	17·390	0·354

In the next series of experiments the air was passed through a plug of silk, formed by rolling a silk handkerchief into a cylindrical shape, and then screwing it into the nozle. The silk weighed 580 grains, and the small quantity of cotton wool placed on the side next the thermometer in order to equalize the stream of air more completely, weighed 15 grains. The stopcock was partly opened as in the experiments of Table II., in order to reduce the pressure to that obtained by passing the full

quantity of air propelled by the pump through a more porous plug. The cylinder of lime was employed.

TABLE IV.—Experiments in which a smaller quantity of air was passed through a plug consisting of 580 grains of silk.

1.	2.	3.	4.	5.	6.	7.	8.
Number of observations from which the results in Columns 4, 6, and 7, are obtained.	Cubic inches passed through the nozle per minute.	Water in 100 grains of air, in grains.	Pressure in lbs. on the square inch.	Atmospheric pressure.	Temperature of the bath.	Temperature of the issuing air.	Cooling effect in Cent. degrees.
10	3071	0·18	33·168	14·727	18°·882	18°·524	0°·358
10	Not observed.	0·18	33·024	14·732	18·884	18·536	0·348
10	Not observed.	0·14	33·820	14·660	19·066	18·686	0·380
10	Not observed.	0·14	33·226	14·650	19·068	18·695	0·373
Mean	.....	0·16	33·309	14·692	18·975	18·610	0·365

TABLE V.—Experiments in which the entire quantity of air propelled by the pump was passed through the silk plug. The cylinder of lime was employed in all excepting the first two experiments.

1.	2.	3.	4.	5.	6.	7.	8.
Number of observations from which the results in Columns 4, 6, and 7, are obtained.	Cubic inches passed through the nozle per minute.	Water in 100 grains of air, in grains.	Pressure in lbs. on the square inch.	Atmospheric pressure.	Temperature of the bath.	Temperature of the issuing air.	Cooling effect in Cent. degrees.
10	7594	0·40	53·722	14·580	17°·585	16°·903	0°·682
10	Not observed.	0·40	53·530	14·580	17·628	16·954	0·674
10	Not observed.	0·32	53·317	14·563	17·993	17·318	0·675
10	Not observed.	0·32	53·317	14·563	18·027	17·357	0·670
10	7742	0·11	55·797	14·615	17·822	17·063	0·759
10	Not observed.	0·11	54·074	14·611	17·813	17·079	0·734
10	Not observed.	0·11	55·720	14·608	17·808	17·082	0·726
10	Not observed.	0·11	56·174	14·605	17·796	17·058	0·738
Mean	.....	0·23	54·456	14·591	17·809	17·102	0·707

In order to obtain a greater pressure, a plug was formed of silk "waste" compressed very tightly into the nozle.

Table VI.—Experiments in which the air, after passing through the cylinder of lime, was forced through a plug consisting of 740 grains of silk.

1. Number of observations from which the results in Columns 4, 6, and 7, are obtained.	2. Cubic inches passed through the nozle per minute.	3. Water in 100 grains of air, in grains.	4. Pressure in lbs. on the square inch.	5. Atmospheric pressure.	6. Temperature of the bath.	7. Temperature of the issuing air.	8. Cooling effect in Cent. degrees.
10	Not observed.	0·19	79·852	14·777	17°·050	15°·884	1°·166
10	Not observed.	0·19	80·133	14·782	17·066	15·913	1·153
10	Not observed.	0·19	79·870	14·787	17·079	15·945	1·134
10	5650	0·19	80·013	14·793	17·083	15·967	1·116
10	Not observed.	0·15	79·814	14·960	16·481	15·338	1·143
10	Not observed.	0·15	80·274	14·957	16·489	15·374	1·115
10	Not observed.	0·15	79·903	14·953	16·505	15·392	1·113
10	5378	0·15	77·867	14·950	16·521	15·428	1·093
10	Not observed.	0·14	78·214	14·638	12·851	11·770	1·081
10	Not observed.	0·14	78·245	14·638	12·877	11·800	1·077
10	Not observed.	0·14	78·180	14·638	12·885	11·824	1·061
10	Not observed.	0·14	78·633	14·638	12·905	11·839	1·066
Mean	.....	0·16	79·250	14·793	15·483	14·373	1·110

In the foregoing experiments the pressure of the air on its exit from the plug was always exactly equal to the atmospheric pressure. To ascertain the effect of an alteration in the pressure of the exit air, we now enclosed a long siphon barometer within the glass tube (fig. 10). The upper part of this tube was surmounted with a cap, furnished with a stopcock, by partially closing which the air at its exit could be brought to the required pressure. The influence of pressure in raising the mercury in the thermometer by compressing its bulb, was ascertained by plunging the instrument into a bottle of water within the glass tube, and noting the amount of the sudden rise or fall of the quicksilver on a sudden augmentation or reduction of pressure. It was found that the pressure equal to that of 17 inches of mercury, raised the indication by 0°·09; which quantity was therefore subtracted after the usual reduction of the thermometric scale.

Table VII.—Experiments with the plug consisting of 740 grains of silk. Pressure of the exit air increased. Cylinder of lime used.

1. Number of observations from which the results in Columns 4, 6, and 7, are obtained.	2. Cubic inches passed through the nozle per minute.	3. Water in 100 grains of air, in grains.	4. Pressure in lbs. on the square inch.	5. Pressure of the exit air.	6. Temperature of the bath.	7. Temperature of the issuing air.	8. Cooling effect in Cent. degrees.
10	Not observed.	0·14	82·982	23·093	12°·673	11°·612	1°·061
10	Not observed.	0·14	82·510	22·878	12·713	11·676	1·037
10	Not observed.	0·14	81·895	22·798	12·755	11·725	1·030
10	Not observed.	0·14	80·630	22·488	12·795	11·792	1·003
Mean	Estimated at 5400	0·14	82·004	22·814	12·734	11·701	1·033

With reference to the experiments in Table VII. it may be remarked, that the cooling effect must be the excess of that which would have been obtained had the air been only resisted by the atmospheric pressure in escaping from the plug, above the cooling effect that would be found in an experiment with the temperature of the bath and the pressure of the entering air the same as the temperature and pressure of the exit air in the actual experiment, and the air issuing at atmospheric pressure. Hence, since two or three degrees of difference of temperature in the bath would not sensibly alter the cooling effect in any of the experiments on air, the cooling effect in an experiment in which the pressure of the exit air is increased, must be sensibly equal to the difference of the cooling effects in two of the ordinary experiments, with the high pressures the same as those used for the entering and issuing air respectively, and the low pressure that of the atmosphere in each case; a conclusion which is verified by the actual results, as the comparison given below shows.

The results recorded in the foregoing Tables are laid down on Chart No. 3, in which the horizontal lines represent the excess of the pressure of the air in the receiver over that of the exit air as found by subtracting the fifth from the fourth columns of the Tables, and the vertical lines represent the cooling effect in tenths of a degree Centigrade. It will be remarked that the line drawn through the points of observation is nearly straight, indicating that the cooling effect is, approximately at least, proportional to the excess of pressure, being about ·018° per pound on the square inch of difference of pressure. Or we may arrive at the same conclusion by dividing the cooling effect (δ) by the difference of pressures ($P-P'$) in the different experiments. We thus find, from the means shown in the different tables,—

Table (I.) $\frac{\delta}{P-P'}$ =	·0170
(II.)	·0179
(III.)	·0165
(IV.)	·0196
(V.)	·0177
(VI.)	·0172
(VII.)	·0174
Mean	·0176

On the Cooling Effects experienced by Carbonic Acid in passing through a porous Plug.

The position of the apparatus gave us considerable practical facilities in experimenting with carbonic acid. A fermenting tun 10 feet deep and 8 feet square was filled with wort to a depth of 6 feet. After the fermentation had been carried on for about forty hours, the gas was found to be produced in sufficient quantity to supply the pump for the requisite time. The carbonic acid was conveyed by a gutta-percha pipe, and passed through two glass vessels surrounded by ice in order to condense the greater portion of vapours. In the succeeding experiment the total quantity of liquid so condensed was 300 grains, which having a specific gravity of ·9965, was composed of 10 grains of alcohol and 290 grains of water. On analysing a portion of the gas during the experiment by passing it through a tube containing chloride of zinc, it was found to contain 0·733 gr. of water to 100 grs. of carbonic acid.

TABLE VIII.—Carbonic acid forced through a plug of 382 grs. of cotton wool. Mean barometric pressure 29·45 inches, equivalent to 14·399 lbs. Gauge under atmospheric pressure 151. The pump was placed in connexion with the pipe immersed in carbonic acid at $10^h\ 55^m$.

1.	2.		3.		4.		5.		6.
Time of observation.	Volume percentage of carbonic acid.		Pressure-gauge; mean pressure in lbs. on the square inch.		Temperature of the bath, by indications of thermometer.		Temperature of the issuing gas, by indications of thermometer.		Cooling effect in Cent. degrees.
h m									
10 47	0		79·0		486·0		198·5		
49	0		79·0		486·0		198·5		
53	0		79·6		486·0		198·2		
57			85·2		486·0		195·0		
58			86·0		486·0		186·0		
59			85·0		486·0		188·6		
11 0	95·51		85·0		486·0		188·5		
2			86·4		486·0		187·6		
4			86·7		486·0		187·8		
6			86·6		486·0		188·9		
9	95·51		86·6		486·0		188·9		
13			84·0		486·0		188·65		
14			84·2	lbs.	486·0		188·1		
15	95·51	94·89	84·4	84·906=32·989	486·0	486·00=20°·001	188·0	188·36=18°·611	1°·390
19			84·5		486·0		188·0		
22			84·1		486·0		188·1		
24			84·6		486·0		188·3		
25	93·03		84·2		486·0		188·5		
28			84·1		486·0		188·6		
32			83·2		486·0		188·9		
33			83·8		486·0		188·9		
35	86·82		84·0		486·0		189·0		
40			83·8		486·0		189·6		
41			83·9		486·0		189·7		
43			85·0		485·9		189·9		
45	79·37	80·61	86·0	84·245=33·286	485·9	485·94=19·998	190·4	190·1 =18·787	1·211
49			84·6		485·9		190·8		
51			84·5		485·9		190·8		
53			83·9		485·9		190·6		
55	75·65		83·6		485·9		190·6		
12 0			83·6		485·9		190·8		
2			83·0		485·7		190·8		
5	70·68		82·7		485·7		190·9		
9		68·82	82·7	82·783=33·960	485·4	485·52=19·980	190·8	191·07=18·884	1·096
13			82·9		485·4		191·1		
15	66·96		82·7		485·5		191·3		
21			82·7		485·4		191·5		
23			82·8		485·4		191·55		
25	65·72		82·9		485·4		191·6		
28			82·9		485·4		191·7		
33			82·2		485·4		191·8		
35	63·23		82·3		485·4		191·7		
40			81·9		485·3		191·65		
44			81·9		485·2		191·6		
45	63·23	63·85	82·1	82·986=33·864	485·2	485·18=19·966	191·6	191·82=18·959	1·007
52			82·4		485·0		191·65		
55	62·0		83·9		485·0		192·0		
1 2			84·1		485·0		192·1		
5	63·23		84·9		485·0		192·1		
11			85·4		485·0		192·3		
15	65·72		82·1		484·9		192·1		

TABLE IX.—Carbonic acid forced through a plug consisting of 191 grs. of cotton wool. Mean barometric pressure 29·6 inches, equivalent to 14·472 lbs. Gauge under atmospheric pressure 150·6. Pump placed in connexion with the pipe immersed in carbonic acid at $10^h\ 38^m$.

1.	2.	3.		4.		5.		6.
Time of observation.	Volume percentage of carbonic acid.	Pressure-gauge, and pressure in lbs. on the square inch equivalent thereto.		Indication of thermometer. Temperature of the bath.		Indication of thermometer. Temperature of the issuing gas.		Cooling effect in Cent. degrees.
h m								
10 40		123·0		461·5		189·5		
42		123·1		461·6		187·6		
44		123·1		461·6		187·25		
50	95·51							
53		123·0		461·75		187·5		
55		123·2	lbs.	461·75		187·45		
57	94·58	123·0	122·91 = 20·43	461·75	461·78 = 18°·962	187·55	187·49 = 18°·522	0·44
59		122·9		461·8		187·55		
11 0	93·65							
1		122·6		461·9		187·55		
3		122·6		461·95		187·6		
5		122·6		462·0		187·55		
7		122·5		462·0		188·1		
9		122·8		462·0		188·1		
10	81·86							
11		122·1		462·0		188·4		
15	76·27	121·6	121·91 = 20·682	462·2	462·11 = 18·976	188·4	188·35 = 18·609	0·367
17		121·7		462·15		188·4		
19		121·6		462·2		188·55		
20	70·68	121·7		462·2		188·7		
21		121·3		462·2		188·65		
25		121·2		462·2		188·7		

In the above, as well as in the next series, the carbonic acid contained 0·35 per cent. of water.

TABLE X.—Experiment in which carbonic acid was forced through a plug consisting of 580 grs. of silk. Mean barometric pressure 29·56, equivalent to 14·452 lbs. Gauge under atmospheric pressure 150·8. Pump placed in connexion with the pipe immersed in carbonic acid at $12^h\ 53^m$. Quantity of gas forced through the plug about 7170 cubic inches per minute.

1. Time of observation.	2. Volume percentage of carbonic acid.	3. Pressure-gauge, and pressure in lbs. on the square inch equivalent thereto.	4. Indication of thermometer. Temperature of the bath.	5. Indication of thermometer. Temperature of the issuing gas.	6. Cooling effect in Cent. degrees.
h s					
12 42	0	52·2	464·2	185·6	
44	0	52·2	464·35	185·5	
46	0	52·2 lbs.	464·4	185·5	
49	0	52·2 = 55·454	464·35	185·55	
50	0	52·2	464·35	185·55	
52	0	52·2	464·4	185·5	
54		56·0	464·55	179·0	
57		55·7	464·65	166·3	
1 0	95·51	56·0	464·3	165·0	
5		56·0	464·55	165·0	
7		56·0	464·5	165·0	
9		56·0	464·4	164·9	
10	96·0 = 94·85	55·92 = 51·7	464·47 = 19·077	165·0 = 16·256	2·821
11		55·8	464·6	164·9	
13		55·6	464·55	164·8	
17		56·0	464·5	165·0	
20	93·03	56·0	464·4	165·4	
24		55·5	464·6	166·0	
25		55·7	464·6	166·3	
27		56·1	464·6	166·8	
30	85·92	56·0 = 55·94 = 51·68	464·7 = 464·71 = 19·088	167·9 = 167·8 = 16·538	2·550
35		56·1	464·8	168·9	
36		56·1	464·8	169·1	
38		56·1	464·9	169·6	

In the above experiment, as well as in those of the adjoining Tables, the sudden diminution of pressure on connecting the pump with the receiver containing carbonic acid, is in perfect accordance with the discovery by Professor GRAHAM of the superior facility with which that gas may be transmitted through a porous body compared with an equal volume of atmospheric air.

TABLE XI.—Experiment in which carbonic acid was forced through a plug consisting of 740 grs. of sik. Mean barometric pressure 30·065, equivalent to 14·723 lbs. on the inch. Gauge under atmospheric pressure 145·65. Pump placed in connexion with the pipe immersed in carbonic acid at $11^h\ 37^m$. Per-centage of moisture in the carbonic acid 0·15.

1.	2.	3.	4.	5.	6.
Time of observation.	Volume per-centage of carbonic acid.	Pressure-gauge, and pressure in lbs. on the square inch equivalent thereto.	Indication of thermometer. Temperature of the bath.	Indication of thermometer. Temperature of the issuing gas.	Cooling effect in Cent. degrees.
h m					
11 28		35·5	318·9	117·9	
30		35·1	318·95	118·0	
32		35·6	318·95	118·0	
34		35·2	318·95	117·9	
36		35·2	318·95	117·73	
37		36·0	318·95	117·5	
38		36·2	318·95	112·0	
39	95·51	36·6		94·0	
43		36·9	319·03	83·95	
45	95·51	37·0		83·6	
47		37·1		83·0	
50	95·51	37·0	319·05	82·6	
53		37·0		82·4	
55	95·51	37·0 lbs.	319·15	82·35	
57	95·51	37·0 = 75·324	319·17 = 12°·844	82·3 82·62 = 7°·974	4°·87
12 0	95·51	37·0		82·7	
2		37·0	319·3	83·0	
5	95·51	37·0		83·0	

In order to ascertain the cooling effect due to pure carbonic acid, we may at present neglect the effect due to the small quantity of watery vapour contained by the gas; and as the cooling effects observed in the various mixtures of atmospheric air and carbonic acid appear nearly consistent with the hypothesis that the specific heats of the two elastic fluids are for equal volumes equal to one another, and that each fluid experiences in the mixture the same absolute thermo-dynamic effect as if the other were removed, we may for the present take the following estimate of the cooling effects due to pure carbonic acid, at the various temperatures and pressures employed, calculated by means of this hypothesis from the observations in which the per-centage of carbonic acid was the greatest, and in fact so great, that a considerable error in the correction for the common air would scarcely affect the result to any sensible extent.

	Temperature of the bath.	Excess of pressure, $P-P'$.	Cooling effect, δ.	Cooling effect divided by excess of pressure.
From Table IX.	18·962	5·958	0·459	·0770
From Table VIII.	20·001	18·590	1·446	·0778
From Table X.	19·077	37·248	2·938	·0789
From Table XI.	12·844	60·601	5·049	·0833
	Mean 17·721			Mean of first three ·0779
				Mean of all .....·0793

We shall see immediately that the temperature of the bath makes a very considerable alteration in the cooling effect, and we therefore select the first three results, obtained at nearly the same temperature, in order to indicate the effect of pressure. On referring to Chart No. 3, it will be remarked that these three results range themselves almost accurately in a straight line. Or, by looking to the numbers in the last column, we arrive at the same conclusion.

Cooling Effect experienced by Hydrogen in passing through a porous Plug.

Not having been able as yet to arrange the large apparatus so as to avoid danger in using this gas in it, we have contented ourselves for the present with obtaining a determination by the help of the smaller force-pump employed in our preliminary experiments. The hydrogen, after passing through a tube filled with fragments of caustic potash, was forced, at a pressure of 68·4 lbs. on the inch, through a piece of leather in contact with the bulb of a small thermometer, the latter being protected from the water of the bath by a piece of india-rubber tube. At a temperature of about 10° Cent., a slight cooling effect was observed, which was found by repeated trials to be 0°·076. The pressure of the atmosphere being 14·7 lbs., it would appear that the cooling effect experienced by this gas is only one-thirteenth of that observed with atmospheric air. We state this result with some reserve, on account of the imperfection of such experiments on a small scale, but there can be no doubt that the effect of hydrogen is vastly inferior to that of atmospheric air.

Influence of Temperature on the Cooling Effect.

By passing steam through pipes plunged into the water of the bath, we were able to maintain it at a high temperature without any considerable variation. The passage of hot air speedily raised the temperature of the stem of the thermometer, as well as of the glass tube in which it was enclosed; but nevertheless the precaution was taken of enclosing the whole in a tin vessel, by means of which water in constant circulation with the water of the bath was kept within one or two inches of the level of the mercury in the thermometer. The bath was completely covered with a wooden lid, and the water kept in constant and vigorous agitation by a proper stirrer.

TABLE XII.—Experiment in which—1st, air; 2nd, carbonic acid; 3rd, air dried by quicklime was forced through a plug consisting of 740 grs. of silk. Mean barometric pressure 30·015, equivalent to 14·68 lbs. on the inch. Gauge under the atmospheric pressure 150. Per-centage of moisture in the carbonic acid 0·31. Pump placed in connexion with the pipe immersed in carbonic acid at $11^h\ 24^m$. Disconnected and attached to the quicklime cylinder at $12^h\ 22^m$.

1.	2.	3.	4.	5.	6.
Time of observation.	Volume per-centage of carbonic acid.	Pressure-gauge, and pressure in lbs. on the square inch equivalent thereto.	Indication of thermometer. Temperature of the bath.	Indication of thermometer. Temperature of the issuing gas.	Cooling effect in Cent. degrees.
h m					
11 5	0	31·6	646·35	479·1	
7	0	31·4	646·3	478·8	
9	0	31·7	646·1	478·05	
11	0	31·6	646·05	478·1	
13	0	31·9	646·05	478·2	
15	0	31·5	646·05	478·35	
17	0	31·8	646·2	478·7	
19	0	31·5	646·0	478·6	
21	0	32·0	646·0	478·7	
22	0	32·2	646·1	478·6	
23	0	32·2	646·1	478·1	
24	0	32·0	646·1	478·8	
25	0	32·0	646·1	477·0	
26	0	32·1	646·4	471·6	
30	95·51	32·2	646·7	469·2	
32	95·51	32·2	646·5	469·5	
33	95·51	32·0	646·45	469·6	
36	95·51	32·6	646·7	469·6	
38	95·51	32·2	646·6	469·9	
40		32·2	646·6	469·98	
43	93·03	32·1	646·6	470·05	
46		32·1	647·0	470·3	
48	90·60	32·1	647·1	470·9	
50		32·1	647·4	471·05	
53	80·82	32·1	647·2	471·2	
55		32·05	647·2	471·75	
58		32·0	647·2	472·05	
12 0	75·65	32·0	647·7	472·6	
4		32·6	647·9	472·9	
6	75·65	32·25	647·8	473·25	
9		32·8	647·95	473·95	
11	65·72	32·4	647·9	474·1	
15	60·83	32·2	647·95	474·8	
20	60·83	32·4	647·95	475·15	
22		32·9	647·95	475·2	
27	0	32·0	647·85	477·0	
29	0	32·0	647·8	480·1	
31	0	31·6	647·5	480·6	
33	0	32·0	647·3	480·6	
35	0	32·1	647·1	480·8	
37	0	32·2	647·0	480·83	
39	0	32·0	647·1	480·9	
41	0	32·1	647·03	481·03	
43	0	32·1	647·1	480·9	
45	0	32·1	647·03	481·02	
47	0	32·4	647·05	481·04	
49	0	32·6	646·98	480·98	
51	0	32·8	646·85	480·9	

2.	3.	4.	5.
95·51			
95·51			
95·51			
95·51	32·23 = 89·799	646·59 = 91·516	469·63 = 88·044
95·51			
93·03			
90·60	32·1 = 90·162	647·03 = 91·579	470·57 = 88·255
80·82			
75·65	32·16 = 90·006	647·5 = 91·647	472·29 = 88·638
75·65			
65·72			
60·83	32·54 = 88·971	647·94 = 91·711	474·64 = 89·162
60·83			
0			
0			
0			
0			
0			
0			
0			
0			
0			
0			
0	32·3 = 89·618	647·02 = 91·578	480·97 = 90·528
0			
0			
0			

2.	3.	4.	5.	6.
62·46	31·62 = 91·508	646·15 = 91·452	478·43 = 90·008	1·444
91·81	31·95 = 90·576	646·08 = 91·442	478·58 = 90·043	1·399
77·37				
62·46				
91·81			

Although hot air had been passed through the plug for half an hour before the readings in the preceding Table were obtained, it is probable that the numbers 1·444 and 1·399, representing the cooling effect of atmospheric air, are not so accurate as the value 1°·050. Taking this latter figure for the effect of an excess of pressure of 89·618 − 14·68 = 74·938 lbs., we find a considerable decrease of cooling effect owing to elevation of temperature, for that pressure, at the low temperatures previously employed, is able to produce a cooling effect of 1°·309.

In order to obtain the effect of carbonic acid unmixed with atmospheric air, we shall, in accordance with the principle already adhered to, consider the thermal capacities of the gases to be equal for equal volumes. Then the cooling effect of the pure gas $= \frac{3{\cdot}472 \times 100 - 1{\cdot}052 \times 4{\cdot}49}{95{\cdot}51} = 3°{\cdot}586$.

Collecting these results, we have,—

Temperature of bath.	Excess of pressure.	Cooling effect.	Cooling effect reduced to 100 lbs. pressure.	Theoretical cooling effect for 100 lbs. pressure.
°		°	°	°
12·844	60·601	5·049	8·33	8·27
19·077	37·248	2·938	7·89	8·07
91·516	74·938	3·586	4·78	4·96

Note.—The numbers shown in the last column of the Table are calculated by the general expression given in our former paper* for the cooling effect, from an empirical formula for the pressure of carbonic acid, recently communicated by Mr. RANKINE in a letter, from which the following is extracted.

"Glasgow, May 9, 1854.

"Annexed I send you formulæ for carbonic acid, in which the coefficient a has been determined *solely* from REGNAULT's experiments on the increase of pressure at constant volume between 0° and 100° Cent. It gives most satisfactory results for expansion at constant pressure, compression at constant temperature, and also (I think) for cooling by free expansion" [*i. e.* the cooling effect in our experiments].

"Carbonic Acid Gas.

P pressure in pounds per square foot.

V volume of one pound in cubic feet.

P_0 one atmosphere.

V_0 *theoretical* volume, in the state of *perfect gas*, of one lb. at the pressure P_0 and the temperature of melting ice.

P_0V_0 for carbonic acid 17116 feet, $\log P_0V_0 = 4{\cdot}2334023$.

(P_0V_0 *actually*, at 0°, 17145.)

K_p dynam. spec. heat at constant pressure 300·7 feet; $\log K_p = 2{\cdot}4781334$.

C absolute temperature of melting ice, 274° Cent.

* Philosophical Transactions, June 1853.

"The absolute zeros of gaseous tension and of heat are supposed sensibly to coincide, i. e. x is supposed inappreciably small.

"*Formulæ*:

$$\frac{PV}{P_0V_0}=\frac{T+C}{C}-\frac{a}{T+C}\cdot\frac{V_0}{V} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$a=1{\cdot}9, \quad \log a=0{\cdot}2787536.$$

"Cooling by free expansion, supposing the perfect gas thermometer to give the true scale of absolute temperatures:

$$\delta T=\frac{P_0V_0}{K_P}\cdot\frac{3a}{T+C}\left\{\frac{V_0}{V_1}-\frac{V_0}{V_2}\right\} \quad . \quad . \quad . \quad . \quad (2)^*$$

$$\log\frac{3P_0V_0a}{K_P}=2{\cdot}5111438."$$

By substituting for $\frac{V_0}{V_1}$ and $\frac{V_0}{V_2}$ their approximate values $\frac{C}{T+C}\cdot\frac{P_1}{P_0}$ and $\frac{C}{T+C}\cdot\frac{P_2}{P_0}$, we reduce it to

$$\delta=\frac{3P_0V_0aC}{K_P(T+C)^2},$$

from which we have calculated the theoretical results for different temperatures shown above, which agree remarkably well with those we have obtained from observation.

The interpretation given above for the experimental results on mixtures of carbonic acid and air depends on the assumption (rendered probable as a very close approximation to the truth, by DALTON's law), that in a mixture each gas retains all its physical properties unchanged by the presence of the other. This assumption, however, may be only approximately true, perhaps similar in accuracy to BOYLE's and GAY-LUSSAC's laws of compression and expansion by heat; and the theory of gases would be very much advanced by accurate comparative experiments on all the physical properties of mixtures and of their components separately. Towards this object we have experimented on the thermal effect of the mutual interpenetration of carbonic acid and air. In one experiment we found that when 7500 cubic inches of carbonic acid at the atmospheric pressure were mixed with 1000 cubic inches of common air and a perfect mutual interpenetration had taken place, the temperature had fallen by about ·2° Cent. We intend to try more exact experiments on this subject.

THEORETICAL DEDUCTIONS.

SECTION I. *On the Relation between the Heat evolved and the Work spent in Compressing a Gas kept at constant temperature.*

This relation is not a relation of simple mechanical equivalence, as was supposed by MAYER† in his 'Bemerkungen ueber die Kräfte der Unbelebten Natur,'

* Obtained by using Mr. RANKINE's formula (1) in the general expression for the cooling effect given in our former paper, and repeated below as equation (15) of Section V.

† Annalen of WÖHLER and LIEBIG, May 1842.

in which he founded on it an attempt to evaluate numerically the mechanical equivalent of the thermal unit. The heat evolved may be less than, equal to, or greater than the equivalent of the work spent, according as the work produces other effects in the fluid than heat, produces only heat, or is assisted by molecular forces in generating heat, and according to the quantity of heat, greater than, equal to, or less than that held by the fluid in its primitive condition, which it must hold to keep itself at the same temperature when compressed. The *à priori* assumption of equivalence, for the case of air, without some special reason from theory or experiment, is not less unwarrantable than for the case of any fluid whatever subjected to compression. Yet it may be demonstrated* that water below its temperature of maximum density (39°·1 FAHR.), instead of evolving any heat at all when compressed, actually absorbs heat, and at higher temperatures evolves heat in greater or less, but probably always very small, proportion to the equivalent of the work spent; while air, as will be shown presently, evolves always, at least when kept at any temperature between 0° and 100° Cent., somewhat more heat than the work spent in compressing it could alone create. The first attempts to determine the relation in question, for the case of air, established an approximate equivalence without deciding how close it might be, or the direction of the discrepance, if any. Thus experiments "On the Changes of Temperature produced by the Rarefaction and Condensation of Air†," showed an approximate agreement between the heat evolved by compressing air into a strong copper vessel under water, and the heat generated by an equal expenditure of work in stirring a liquid; and again, conversely, an approximate compensation of the cold of expansion when air in expanding spends all its work in *stirring* its own mass by rushing through the narrow passage of a slightly opened stopcock. Again, theory‡, without any doubtful hypothesis, showed from REGNAULT's observations on the pressure and latent heat of steam, that unless the density of saturated steam differs very much from what it would be if following the gaseous laws of expansion and compression, the heat evolved by the compression of air must be sensibly less than the equivalent of the work spent when the temperature is as low as 0° Cent., and very considerably greater than that equivalent when the temperature is above 40° or 50°. Mr. RANKINE is, so far as we know, the only other writer who independently admitted the necessity of experiment on the subject, and he was probably not aware of the experiments which had been made in 1844, on the rarefaction and condensation of air, when he remarked§, that "the value of $\varkappa$ is

* Dynamical Theory of Heat, § 63, equation (*b*.), Trans. Roy. Soc. Edinb. vol. xvi. p. 290; or Phil. Mag. vol. iv. Series 4. p. 425.

† Communicated to the Royal Society, June 20, 1844, and published in the Philosophical Magazine, May 1845.

‡ Appendix to "Account of CARNOT's Theory," Roy. Soc. Edinburgh, April 30, 1849, Transactions, vol. xvi. p. 568; confirmed in the Dynamical Theory, § 22, Transactions Roy. Soc. Edinb. March 17, 1851; and Phil. Mag. vol. iv. Series 4. p. 20.

§ Mechanical Action of Heat, Section II. (10.), communicated to the Roy. Soc Edinb. Feb. 4, 1850, Transactions, vol. xx. p. 166.

unknown; and as yet no experimental data exist by which it can be determined" ($\varkappa$ denoting in his expressions a quantity the vanishing of which for any gas would involve the equivalence in question). In further observing that probably $\varkappa$ is small in comparison with the reciprocal of the coefficient of expansion, Mr. RANKINE virtually adopted the equivalence as probably approximate; but in his article "On the Thermic Phenomena of Currents of Elastic Fluids*," he took the first opportunity of testing it closely, afforded by our preliminary experiments on the thermal effects of air escaping through narrow passages.

We are now able to give much more precise answers to the question regarding the heat of compression, and to others which rise from it, than those preliminary experiments enabled us to do. Thus if K denote the specific heat under constant pressure, of air or any other gas, issuing from the plug in the experiments described above, the quantity of heat that would have to be supplied, per pound of the fluid passing, to make the issuing stream have the temperature of the bath, would be $K\delta$, or

$$Km\frac{(P-P')}{\Pi},$$

where m is equal to ·26° for air and 1·15° for carbonic acid, since we found that the cooling effect was simply proportional to the difference of pressure in each case, and was ·0176° per pound per square inch, or ·26 per atmosphere, for air, and about 4½ times as much for carbonic acid. This shows precisely how much the heat of friction in the plug falls short of compensating the cold of expansion. But the heat of friction is the thermal equivalent of all the work done actually in the narrow passages by the air expanding as it flows through. Now this, in the cases of air and carbonic acid, is really not as much as the whole work of expansion, on account of the deviation from BOYLE's law to which these gases are subject; but it exceeds the whole work of expansion in the case of hydrogen which presents a contrary deviation; since P'V', the work which a pound of air must do to escape against the atmospheric pressure, is, for the two former gases, rather greater, and for hydrogen rather less, than PV, which is the work done on it in pushing it through the spiral up to the plug. In any case, w denoting the whole work of expansion, $w-(P'V'-PV)$ will be the work actually spent in friction within the plug; and

$$\frac{1}{J}\{w-(P'V'-PV)\}$$

will be the quantity of heat into which it is converted, a quantity which, in the cases of air and carbonic acid, falls short by

$$Km\frac{P-P'}{\Pi}$$

of compensating the cold of expansion. If therefore H denote the quantity of heat

* Mechanical Action of Heat, Subsection 4, communicated to the Roy. Soc. Edinb. Jan. 4, 1853, Transactions, vol. xx. p. 580.

that would exactly compensate the cold of expansion, or which amounts to the same, the quantity of heat that would be evolved by compressing a pound of the gas from the volume V' to the volume V, when kept at a constant temperature, we have

$$\frac{1}{J}\{w-(P'V'-PV)\}=H-Km\frac{P-P'}{\Pi},$$

whence

$$H=\frac{w}{J}+\left\{-\frac{1}{J}(P'V'-PV)+Km\frac{P-P'}{\Pi}\right\}.$$

Now, from the results derived by Regnault from his experiments on the compressibility of air, of carbonic acid, and of hydrogen, at three or four degrees above the freezing-point, we find, approximately,

$$\frac{P'V'-PV}{PV}=f\frac{P-P'}{\Pi},$$

where $f=$ ·00082 for air,
$f=$ ·0064 for carbonic acid,
and $f=-$·00043 for hydrogen.

No doubt the deviations from Boyle's law will be somewhat different at the higher temperature (about 15° or 16° Cent.) of the bath in our experiments, probably a little smaller for air and carbonic acid, and possibly greater for hydrogen; but the preceding formula may express them accurately enough for the rough estimate which we are now attempting.

We have, therefore, for air or carbonic acid,

$$H=\frac{w}{J}+\left(Km-\frac{PVf}{J}\right)\frac{P-P'}{\Pi}=\frac{w}{J}+\frac{PV}{J}\left(\frac{JKm}{PV}-f\right)\frac{P-P'}{\Pi}.$$

The values of JK and PV for the three gases in the circumstances of the experiments are as follow:—

For atmospheric air $JK=1390\times$ ·238 $=331$
For carbonic acid $JK=1390\times$ ·217 $=301$
For hydrogen . . $JK=1390\times3{\cdot}4046=4732$

and for atmospheric air, at 15° Cent. $PV=26224(1+15\times{\cdot}00366)=27663$
for carbonic acid, at 10° Cent. $PV=17154(1+10\times{\cdot}00366)=17782$
for hydrogen . . at 10° Cent. $PV=378960(1+10\times{\cdot}00367)=393000$.

Hence we have, for air and carbonic acid,

$$H=\frac{w}{J}+\frac{PV}{J}\cdot\lambda\frac{P-P'}{\Pi},$$

where λ denotes ·0024 for air, and ·013 for carbonic acid; showing (since these values of λ are positive) that in the case of each of these gases, more heat is evolved in compressing it than the equivalent of the work spent (a conclusion that would hold for hydrogen even if no cooling effect, or a heating effect less than a certain limit, were observed for it in our form of experiment). To find the proportion which this excess bears to the whole heat evolved, or to the thermal equivalent of the work spent

in the compression, we may use the expression

$$w = PV \log \frac{P}{P'},$$

as approximately equal to the mechanical value of either of those energies; and we thus find for the proportionate excess,

$$\frac{H - \frac{1}{J}w}{\frac{1}{J}w} = \lambda \frac{P - P'}{\Pi \log \frac{P}{P'}} = \cdot 0024 \frac{P - P'}{\Pi \log \frac{P}{P'}} \text{ for air,}$$

or

$$= \cdot 013 \frac{P - P'}{\Pi \log \frac{P}{P'}} \text{ for carbonic acid.}$$

This equation shows in what proportion the heat evolved exceeds the equivalent of the work spent in any particular case of compression of either gas. Thus for a very small compression from $P' = \Pi$, the atmospheric pressure, we have

$$\log \frac{P}{P'} = \log \left(1 + \frac{P - \Pi}{\Pi}\right) = \frac{P - \Pi}{\Pi} \text{ approximately,}$$

and therefore

$$\frac{H - \frac{1}{J}w}{\frac{1}{J}w} = \cdot 0024 \text{ for air,}$$

or

$$= \cdot 013 \text{ for carbonic acid.}$$

Therefore, when slightly compressed from the ordinary atmospheric pressure, and kept at a temperature of about 60° FAHR., common air evolves more heat by $\frac{1}{417}$, and carbonic acid more by $\frac{1}{77}$ than the amount mechanically equivalent to the work of compression. For considerable compressions from the atmospheric pressure, the proportionate excesses of the heat evolved are greater than these values, in the ratio of the Napierian logarithm of the number of times the pressure is increased, to this number diminished by 1. Thus, if either gas be compressed from the standard state to double density, the heat evolved exceeds the thermal equivalent of the work spent, by $\frac{1}{290}$ in the case of air, and by $\frac{1}{53}$ in the case of carbonic acid.

As regards these two gases, it appears that the observed cooling effect was chiefly due to an actual preponderance of the mechanical equivalent of the heat required to compensate the cold of expansion over the work of expansion, but that rather more than one-fourth of it in the case of air, and about one-third of it in the case of carbonic acid, depended on a portion of the work of expansion going to do the extra work spent by the gas in issuing against the atmospheric pressure above that gained by it in being sent into the plug. On the other hand, in the case of hydrogen, in such an experiment as we have performed, there would be a heating effect, if the

work of expansion were precisely equal to the mechanical equivalent of the cold of expansion, since not only the whole work of expansion, but also the excess of the work done in forcing the gas in above that performed by it in escaping, is spent in friction in the plug. Since we have observed actually a cooling effect, it follows that the heat absorbed in expansion must exceed the equivalent of the work of expansion, enough to over-compensate the whole heat of friction mechanically equivalent, as this is, to the work of expansion together with the extra work of sending the gas into the plug above that which it does in escaping. In the actual experiment* we found a cooling effect of ·076°, with a difference of pressures, P−P′, equal to 53·7 lbs. per square inch, or 3·7 atmospheres. Now the mechanical value of the specific heat of a pound of hydrogen is, according to the result stated above, 4732 foot-pounds, and hence the mechanical value of the heat that would compensate the observed cooling effect per pound of hydrogen passing is 360 foot-pounds. But, according to Regnault's experiments on the compression of hydrogen, quoted above, we have

$$PV-P'V'=PV\times\cdot00043\frac{P-P'}{\Pi}\text{ approximately;}$$

and as the temperature was about 10° in our experiment, we have, as stated above, PV=393000.

Hence, for the case of the experiment in which the difference of pressures was 3·7 atmospheres, or

$$\frac{P-P'}{\Pi}=3\cdot7,$$

we have

$$PV-P'V'=625;$$

that is, 625 foot-pounds more of work, per pound of hydrogen, is spent in sending the hydrogen into the plug at 4·7 atmospheres of pressure, than would be gained in allowing it to escape at the same temperature against the atmospheric pressure. Hence the heat required to compensate the cold of expansion, is generated by friction from (1) the actual work of expansion, together with (2) the extra work of 625 foot-pounds per pound of gas, and (3) the amount equivalent to 360 foot-pounds which would have to be communicated from without to do away with the residual cooling effect observed. Its mechanical equivalent therefore exceeds the work of expansion by 985 foot-pounds; which is $\frac{1}{630}$ of its own amount, since the work of expansion in the circumstances is approximately $393000\times\log 4\cdot7=608000$ foot-pounds. Conversely, the heat evolved by the compression of hydrogen at 10° Cent., from 1 to 4·7 atmospheres, exceeds by $\frac{1}{630}$ the work spent. The corresponding excess in the case

* From the single experiment we have made on hydrogen we cannot conclude that at other pressures a cooling effect proportional to the difference of pressures would be observed, and therefore we confine the comparison of the three gases to the particular pressure used in the hydrogen experiment. It should be remarked too, that we feel little confidence in the value assigned to the thermal effect for the case observed in the experiment on hydrogen, and only consider it established that it is a cooling effect, and very small.

of atmospheric air, according to the result obtained above, is $\frac{1}{174}$, and in the case of carbonic acid $\frac{1}{32}$.

It is important to observe how much less close is the compensation in carbonic acid than in either of the other gases, and it appears probable that the more a gas deviates from the gaseous laws, or the more it approaches the condition of a vapour at saturation, the wider will be the discrepancy. We hope, with a view to investigating further the physical properties of gases, to extend our method of experimenting to steam (which will probably present a large cooling effect), and perhaps to some other vapours.

In Mr. JOULE's original experiment* to test the relation between heat evolved and work spent in the compression of air, without an independent determination of the mechanical equivalent of the thermal unit, air was allowed to expand through the aperture of an open stopcock from one copper vessel into another previously exhausted by an air-pump, and the whole external thermal effect on the metal of the vessels, and a mass of water below which they are kept, was examined. We may now estimate the actual amount of that external thermal effect, which observation only showed to be insensibly small. In the first place it is to be remarked, that, however the equilibrium of pressure and temperature is established between the two air vessels, provided only no appreciable amount of work is emitted in sound, the same quantity of heat must be absorbed from the copper and water to reduce them to their primitive temperature; and that this quantity, as was shown above, is equal to

$$\frac{PV}{J}\times\cdot0024\times\frac{P-P'}{\Pi}=\frac{27000\times\cdot0024}{1390}\times\frac{P-P'}{\Pi}=\cdot046\frac{P-P'}{\Pi}.$$

In the actual experiments the exhausted vessel was equal in capacity to the charged vessel, and the latter contained ·13 of a pound of air under 21 atmospheres of pressure, at the commencement. Hence $P'=\frac{1}{2}P$, and

$$\frac{P-P'}{\Pi}=10\cdot5;$$

and the quantity of heat required from without to compensate the total internal cooling effect must have been

$$\cdot046\times10\cdot5\times\cdot13=\cdot063.$$

This amount of heat, taken from $16\frac{1}{2}$ lbs. of water, 28 lbs. of copper, and 7 lbs. of tinned iron, as in the actual experiment, would produce a lowering of temperature of only ·003° Cent. We need not therefore wonder that no sensible external thermal effect was the result of the experiment when the two copper vessels and the pipe connecting them were kept under water, stirred about through the whole space

* The second experiment mentioned in the abstract published in the Proceedings of the Royal Society, June 20, 1844, and described in the Philosophical Magazine, May 1845, p. 377.

surrounding them, and that similar experiments, more recently made by M. REGNAULT, should have led only to the same negative conclusion.

If, on the other hand, the air were neither allowed to take in heat from nor to part with heat to the surrounding matter in any part of the apparatus, it would experience a resultant cooling effect (after arriving at a state of uniformity of temperature as well as pressure) to be calculated by dividing the preceding expression for the quantity of heat which would be required to compensate it, by ·17, the specific heat of air under constant pressure. The cooling effect on the air itself therefore amounts to

$$0°{\cdot}27 \times \frac{P-P'}{\Pi},$$ *

which is equal to 2°·8, for air expanding, as in Mr. JOULE's experiment, from 21 atmospheres to half that pressure, and is 900 times as great as the thermometric effect when spread over the water and copper of the apparatus. Hence our present system, in which the thermometric effect on the air itself is directly observed, affords a test hundreds of times more sensitive than the method first adopted by Mr. JOULE, and no doubt also than that recently practised by M. REGNAULT, in which the dimensions of the various parts of the apparatus (although not yet published) must have been on a corresponding scale, or in somewhat similar proportions, to those used formerly by Mr. JOULE.

SECTION II. *On the Density of Saturated Steam.*

The relation between the heat evolved and the work spent, approximately established by the air-experiments communicated to the Royal Society in 1844, was subjected to an independent indirect test by an application of CARNOT's theory, with values of "CARNOT's function" which had been calculated from REGNAULT's data as to the pressure and latent heat of steam, and the assumption (in want of experimental data), that the density varies according to the gaseous laws. The verification thus obtained was very striking, showing an exact agreement with the relation of equivalence at a temperature a little above that of observation, and an agreement with the actual experimental results quite within the limits of the errors of observation; but a very wide discrepancy from equivalence for other temperatures. The following Table is extracted from the Appendix to the "Account of CARNOT's Theory" in which the theoretical comparison was first made, to facilitate a comparison with what we now know to be the true circumstances of the case.

* It is worthy of remark that this, the expression for the cooling effect experienced by a mass of atmospheric air expanding from a bulk in which its pressure is P to a bulk in which, at the same (or very nearly the same) temperature its pressure is P', and spending all its work of expansion in friction among its own particles, agrees very closely with the expression, $·26 \times \frac{P-P'}{\Pi}$, for the cooling effect in the somewhat different circumstances of our experiments.

"Table of the Values of $\frac{\mu(1+Et)}{E}=[W]$.

"Work requisite to produce a unit of heat by the compression of a gas $\frac{[\mu](1+Et)}{E}=[W]$.	"Temperature of the gas t.	"Work requisite to produce a unit of heat by the compression of a gas $\frac{[\mu](1+Et)}{E}=[W]$.	"Temperature of the gas t.
ft. lbs.	°	ft. lbs.	°
1357·1	0	1446·4	120
1368·7	10	1455·8	130
1379·0	20	1465·3	140
1388·0	30	1475·8	150
1395·7	40	1489·2	160
1401·8	50	1499·0	170
1406·7	60	1511·3	180
1412·0	70	1523·5	190
1417·6	80	1536·5	200
1424·0	90	1550·2	210
1430·6	100	1564·0	220
1438·2	110	1577·8	230"

We now know, from the experiments described above in the present paper, that the numbers in the first column, and we may conclude with almost equal certainty, that the numbers in the third also, ought to be each very nearly the mechanical equivalent of the thermal unit. This having been ascertained to be 1390 (for the thermal unit Centigrade) by the experiments on the friction of fluids and solids, communicated to the Royal Society in 1849, and the work having been found above to fall short of the equivalent of heat produced, by about $\frac{1}{417}$, at the temperature of the air-experiments at present communicated, and by somewhat less at such a higher temperature as 30°, we may infer that the agreement of the tabulated theoretical result with the fact is perfect at about 30° Cent. Or, neglecting the small discrepance by which the work truly required falls short of the equivalent of heat produced, we may conclude that the true value of $\frac{\mu(1+Et)}{E}$ for all temperatures is about 1390; and hence that if $[W]$ denote the numbers shown for it in the preceding table, μ the true value of Carnot's function, and $[\mu]$ the value tabulated for any temperature in the "Account of Carnot's Theory," we must have, to a very close degree of approximation,

$$\mu=[\mu]\times\frac{1390}{[W]}.$$

But if $[\sigma]$ denote the formerly assumed specific gravity of saturated steam, p its pressure, and λ its latent heat per pound of matter, and if ϱ be the mass (in pounds) of water in a cubic foot, the expression from which the tabulated values of $[\mu]$ were calculated is

$$[\mu]=\frac{1-[\sigma]}{\varrho[\sigma]}\frac{1}{\lambda}\frac{dp}{dt};$$

while the true expression for Carnot's function in terms of properties of steam is

$$\mu=\frac{1-\sigma}{\varrho\sigma}\cdot\frac{1}{\lambda}\frac{dp}{dt}.$$

Hence $$\frac{\mu}{[\mu]}=\frac{[\sigma]}{\sigma}\cdot\frac{1-\sigma}{1-[\sigma]};$$

or, approximately, since σ and $[\sigma]$ are small fractions,

$$\frac{\mu}{[\mu]}=\frac{[\sigma]}{\sigma}.$$

We have, therefore, $$\frac{\sigma}{[\sigma]}=\frac{[W]}{1390};$$

and we infer that the densities of saturated steam in reality bear the same proportions to the densities assumed, according to the gaseous laws, as the numbers shown for different temperatures in the preceding Table bear to 1390. Thus we see that the assumed density must have been very nearly correct, about 30° Cent., but that the true density increases much more at the high temperatures and pressures than according to the gaseous laws, and consequently that steam appears to deviate from Boyle's law in the same direction as carbonic acid, but to a much greater amount, which in fact it must do unless its coefficient of expansion is very much less, instead of being, as it probably is, somewhat greater than for air. Also, we infer that the specific gravity of steam at 100° Cent., instead of being only $\frac{1}{1693\cdot5}$, as was assumed, or about $\frac{1}{1700}$, as it is generally supposed to be, must be as great as $\frac{1}{1645}$. Without using the preceding Table, we may determine the absolute density of saturated steam by means of a formula obtained as follows. Since we have seen the true value of W is nearly 1390, we must have, very approximately,

$$\mu=\frac{1390\,\mathrm{E}}{1+\mathrm{E}t},$$

and hence, according to the preceding expression for μ in terms of the properties of steam,

$$\varrho\sigma=\frac{1-\sigma}{1390\,\mathrm{E}}(1+\mathrm{E}t)\,\frac{1}{\lambda}\frac{dp}{dt},$$

or, within the degree of approximation to which we are going (omitting as we do fractions such as $\frac{1}{400}$ of the quantity evaluated),

$$\varrho\sigma=\frac{(1+\mathrm{E}t)}{1390\,\mathrm{E}.\lambda}\frac{dp}{dt},$$

an equation by which $\varrho\sigma$, the mass of a cubic foot of steam in fraction of a pound, or ν, its specific gravity (the value of ϱ being 63·887), may be calculated from observations such as those of Regnault on steam. Thus, using Mr. Rankine's empirical formula for the pressure which represents M. Regnault's observations correctly at all temperatures, and M. Regnault's own formula for the latent heat; and taking $\mathrm{E}=\frac{1}{273}$,

we have $$\varrho\sigma=\frac{273+t}{1390}\,\frac{p\left(\frac{\beta}{(274\cdot6+t)^2}+\frac{2\gamma}{(274\cdot6+t)^3}\right)\times\cdot4342945}{(606\cdot5+0\cdot305t)-(t+\cdot00002t^2+\cdot0000003t^3)},$$

with the following equations for calculating p and the terms involving β and γ;

$$\log_{10} p = \alpha - \frac{\beta}{t+274{\cdot}6} - \frac{\gamma}{(274{\cdot}6+t)^2},$$

$$\alpha = 4{\cdot}950433 + \log_{10} 2114 = 8{\cdot}275538$$

$$\log_{10} \beta = 3{\cdot}1851091,$$

$$\log_{10} \gamma = 5{\cdot}0827176.$$

The densities of saturated steam calculated for any temperatures, either by means of this formula, or by the expression given above, with the assistance of the Table of values of [W], are the same as those which, in corresponding on the subject in 1848, we found would be required to reconcile REGNAULT's actual observations on steam with the results of air-experiments which we then contemplated undertaking, should they turn out, as we now find they do, to confirm the relation which the air-experiments of 1844 had approximately established. They should agree with results which CLAUSIUS* gave as a consequence of his extension of CARNOT's principle to the dynamical theory of heat, and his assumption of MAYER's hypothesis.

SECTION III. *Evaluation of* CARNOT's *Function.*

The importance of this object, not only for calculating the efficiency of steam-engines and air-engines, but for advancing the theory of heat and thermo-electricity, was a principal reason inducing us to undertake the present investigation. Our preliminary experiments, demonstrating that the cooling effect which we discovered in all of them was very slight for a considerable variety of temperatures (from about 0° to 77° Cent.), were sufficient to show, as we have seen in §§ I. and II., that $\frac{\mu(1+Et)}{E}$ must be very nearly equal to the mechanical equivalent of the thermal unit; and therefore we have

$$\mu = \frac{J}{\frac{1}{E}+t} \text{ approximately,}$$

or, taking for E the standard coefficient of expansion of atmospheric air, ·003665,

$$\mu = \frac{J}{272{\cdot}85+t}.$$

At the commencement of our first communication to the Royal Society on the subject, we proposed to deduce more precise values for this function by means of the equation

$$\frac{J}{\mu} = \frac{JK\delta - (P'V' - PV) + w}{\frac{dw}{dt}};$$

where

$$w = \int_V^{V'} p\,dv;$$

* POGGENDORFF's Annalen, April and May 1850.

v, V, V′ denote, with reference to air at the temperature of the bath, respectively, the volumes occupied by a pound under any pressure p, under a pressure, P, equal to that with which the air enters the plug, and under a pressure, P′, with which the air escapes from the plug; and JKδ is the mechanical equivalent of the amount of heat per pound of air passing that would be required to compensate the observed cooling effect δ. The direct use of this equation for determining $\frac{J}{\mu}$ requires, besides our own results, information as to compressibility and expansion which is as yet but very insufficiently afforded by direct experiments, and is consequently very unsatisfactory, so much so that we shall only give an outline, without details, of two plans we have followed, and mention the results. First, it may be remarked that, approximately,

$$w=(1+\mathrm{E}t)\mathrm{H}\log\frac{\mathrm{P}}{\mathrm{P}'},\text{ and }\frac{dw}{dt}=\mathrm{EH}\log\frac{\mathrm{P}}{\mathrm{P}'},$$

H being the "height of the homogeneous atmosphere," or the product of the pressure into the volume of a pound of air, at 0° Cent.; of which the value is 26224 feet. Hence, if **E** denote a certain mean coefficient of expansion suitable to the circumstances of each individual experiment, it is easily seen that $\frac{w}{\frac{dw}{dt}}$ may be put under the form $\frac{1}{\mathbf{E}}+t$, and thus we have

$$\frac{\mathrm{J}}{\mu}=\frac{1}{\mathbf{E}}+t+\frac{\mathrm{JK}\delta-(\mathrm{P}'\mathrm{V}'-\mathrm{PV})}{\mathrm{EH}\log\frac{\mathrm{P}}{\mathrm{P}'}},$$

since the numerator of the fraction constituting the last term is so small, that the approximate value may be used for the denominator. The first term of the second member may easily be determined analytically in general terms; but as it has reference to the rate of expansion at the particular temperature of the experiment, and not to the mean expansion from 0° to 100°, which alone has been investigated by Regnault and others who have made sufficiently accurate experiments, we have not data for determining its values for the particular cases of the experiments. We may, however, failing more precise data, consider the expansion of air as uniform from 0° to 100°, for any pressure within the limits of the experiments (four or five atmospheres); because it is so for air at the atmospheric density by the hypothesis of the air-thermometer, and Regnault's comparisons of air-thermometers in different conditions show for all, whether on the constant-volume or constant-pressure principle, with density or pressure from one-half to double the standard density or pressure, a very close agreement with the standard air-thermometer. On this assumption then, when we take into account Regnault's observations regarding the effect of variations of density on the coefficient of increase of pressure, we find that a suitable mean coefficient **E** for the circumstances of the preceding formula for $\frac{\mathrm{J}}{\mu}$ is expressed,

to a sufficient degree of approximation, by the equation

$$E=\cdot0036534+\frac{\cdot0000441}{3\cdot81}\frac{P-P'}{\Pi\log\frac{P}{P'}}.$$

Also, by using REGNAULT's experimental results on compressibility of air as if they had been made, not at 4°·75, but at 16° Cent., we have estimated $P'V'-PV$ for the numerator of the last term of the preceding expression. We have thus obtained estimates for the value of $\frac{J}{\mu}$, from eight of our experiments (not corresponding exactly to the arrangement in seven series given above), which, with the various items of the correction in the case of each experiment, are shown in the following Table.

No. of experiment.	Pressure of air forced into the plug.	Barometric pressure.	Excess.	Cooling effect.	Correction by cooling effect.	Correction by reciprocal coefficient of expansion.	Correction by compressibility (subtracted).	Value of J divided by CARNOT's function for 16° Cent.
	P.	P'.	P−P'.	δ.	$\frac{JK\delta}{EH\log\frac{P}{P'}}$	$\frac{1}{E}-\frac{1}{E'}$	$\frac{P'V'-PV}{EH\log\frac{P}{P'}}$	$\frac{J}{\mu_{16}}$
I.	20·943	14·777	6·166	0·105	1·031	0·174	0·290	289·4
II.	21·282	14·326	6·956	0·109	0·942	0·168	0·291	289·3
III.	35·822	14·504	21·318	0·375	1·421	0·519	0·412	289·97
IV.	33·310	14·692	18·618	0·364	1·523	0·470	0·372	290·065
V.	55·441	14·610	40·831	0·740	1·892	0·923	0·480	289·705
VI.	53·471	14·571	38·900	0·676	1·814	0·883	0·475	289·59
VII.	79·464	14·955	64·509	1·116	2·272	1·379	0·592	289·69
VIII.	79·967	14·785	65·182	1·142	2·300	1·376	0·586	289·73
							Mean ...	289·68

In consequence of the approximate equality of $\frac{J}{\mu}$ to $\frac{1}{E}+t$, its value must be, within a very minute fraction, less by 16 at 0° than at 16°; and, from the mean result of the preceding Table, we therefore deduce 273·68 as the value of $\frac{J}{\mu}$ at the freezing-point. The correction thus obtained on the approximate estimate $\frac{1}{E}+t=272\cdot85+t$, for $\frac{J}{\mu}$, at temperatures not much above the freezing-point, is an augmentation of ·83.

For calculating the unknown terms in the expression for $\frac{J}{\mu}$, we have also used Mr. RANKINE's formula for the pressure of air, which is as follows:—

$$pv=H\frac{C+t}{C}\left\{1-\frac{aC}{(C+t)^3}\left(\frac{1}{\varrho v}\right)^{\frac{1}{2}}+\frac{hC}{C+t}\left(\frac{1}{\varrho v}\right)^{\frac{1}{3}}\right\},$$

where $C=274\cdot6$, $\log_{10}a=\cdot3176168$, $\log_{10}h=\bar{3}\cdot8181546$,

$$H=\frac{26224}{1-a+h};$$

and, v being the volume of a pound of air when at the temperature t and under the pressure p, ϱ denotes the mass in pounds of a cubic foot at the standard atmospheric pressure of 29·9218 inches of mercury. The value of p according to this equation,

when substituted in the general expression for $\frac{J}{\mu}$, gives

$$\frac{J}{\mu}=C+t+\frac{\frac{JKC}{H}\delta+3h\frac{C^3}{(C+t)^4}\left\{\left(\frac{P}{\Pi}\right)^{\frac{4}{3}}-\left(\frac{P'}{\Pi}\right)^{\frac{4}{3}}\right\}-\frac{13}{3}a\left(\frac{C}{C+t}\right)^{\frac{4}{3}}\left\{\left(\frac{P}{\Pi}\right)^{\frac{4}{3}}-\left(\frac{P'}{\Pi}\right)^{\frac{4}{3}}\right\}}{\log\frac{P}{P'}}.$$

From this we find, with the data of the eight experiments just quoted, the following values for $\frac{J}{\mu}$ at the temperature 16° Cent.,

289·044, 289·008, 288·849, 289·112, 288·787, 288·722, 288·505, 288·559, the mean of which is 288·82,

giving a correction of only ·03 to be subtracted from the previous approximate estimate $\frac{1}{E}+t$.

It should be observed that CARNOT's function varies only with the temperature; and therefore if such an expression as the preceding, derived from Mr. RANKINE's formula, be correct, the cooling effect, δ, must vary with the pressure and temperature in such a way as to reduce the complex fraction, constituting the second term, to either a constant or a function of t. Now at the temperature of our experiments, δ is very approximately proportional simply to $P-P'$, and therefore all the terms involving the pressure in the numerator ought to be either linear or logarithmic; and the linear terms should balance one another so as to leave only terms which, when divided by $\log\frac{P}{P'}$, become independent of the pressures. This condition is not fulfilled by the actual expression, but the calculated results agree with one another as closely as could be expected from a formula obtained with such insufficient experimental data as Mr. RANKINE had for investigating the empirical forms which his theory left undetermined. We shall see in Section V. below, that simpler forms represent REGNAULT's data within their limits of error of observation, and at the same time may be reduced to consistency in the present application.

As yet we have no data regarding the cooling effect, of sufficient accuracy for attempting an independent evaluation of CARNOT's function for other temperatures. In the following section, however, we propose a new system of thermometry, the adoption of which will quite alter the form in which such a problem as that of evaluating CARNOT's function for any temperature presents itself.

SECTION IV. *On an absolute Thermometric Scale founded on the Mechanical Action of Heat.*

In a communication to the Cambridge Philosophical Society* six years ago, it

* "On an Absolute Thermometric Scale founded on CARNOT's Theory of the Motive Power of Heat, and calculated from REGNAULT's observations on Steam," by Prof. W. THOMSON, Proceedings Camb. Phil. Soc. June 5, 1848, or Philosophical Magazine, Oct. 1848.

was pointed out that any system of thermometry, founded either on equal additions of heat, or equal expansions, or equal augmentations of pressure, must depend on the particular thermometric substance chosen, since the specific heats, the expansions, and the elasticities of substances vary, and, so far as we know, not proportionally with absolute rigour for any two substances. Even the air-thermometer does not afford a *perfect standard*, unless the precise constitution and physical state of the gas used (the density, for a pressure-thermometer, or the pressure, for an expansion-thermometer) be prescribed; but the very close agreement which REGNAULT found between different air- and gas-thermometers removes, for all practical purposes, the inconvenient narrowness of the restriction to atmospheric air kept permanently at its standard density, imposed on the thermometric substance in laying down a rigorous definition of temperature. It appears then that the standard of practical thermometry consists essentially in the reference to a certain numerically expressible quality of a particular substance. In the communication alluded to, the question, "Is there any principle on which an absolute thermometric scale can be founded?" was answered by showing that CARNOT's function (derivable from the properties of any substance whatever, but the same for all bodies at the same temperature), or any arbitrary function of CARNOT's function, may be defined as temperature, and is therefore the foundation of an absolute system of thermometry. We may now adopt this suggestion with great advantage, since we have found that CARNOT's function varies very nearly in the inverse ratio of what has been called "temperature from the zero of the air-thermometer," that is, Centigrade temperature by the air-thermometer increased by the reciprocal of the coefficient of expansion; and we may define temperature simply as the reciprocal of CARNOT's function. When we take into account what has been proved regarding the mechanical action of heat*, and consider what is meant by CARNOT's function, we see that the following explicit definition may be substituted:—

If any substance whatever, subjected to a perfectly reversible cycle of operations, takes in heat only in a locality kept at a uniform temperature, and emits heat only in another locality kept at a uniform temperature, the temperatures of these localities are proportional to the quantities of heat taken in or emitted at them in a complete cycle of the operations.

To fix on a unit or degree for the numerical measurement of temperature, we may either call some definite temperature, such as that of melting ice, unity, or any number we please; or we may choose two definite temperatures, such as that of melting ice and that of saturated vapour of water under the pressure 29·9218 inches of mercury in the latitude 45°, and call the difference of these temperatures any number we please, 100 for instance. The latter assumption is the only one that can be made conveniently in the present state of science, on account of the necessity of retaining a connexion with practical thermometry as hitherto practised; but the former is far

* Dynamical Theory of Heat, §§ 42, 43.

preferable in the abstract, and must be adopted ultimately. In the mean time it becomes a question, what is the temperature of melting ice, if the difference between it and the standard boiling-point be called 100°? When this question is answered within a tenth of a degree or so, it may be convenient to alter the foundation on which the degree is defined, by assuming the temperature of melting ice to agree with that which has been found in terms of the old degree; and then to make it an object of further experimental research, to determine by what minute fraction the range from freezing to the present standard boiling-point exceeds or falls short of 100. The experimental data at present available do not enable us to assign the temperature of melting ice, according to the new scale, to perfect certainty within less than two- or three-tenths of a degree; but we shall see that its value is probably about 273·7, agreeing with the value of $\frac{J}{\mu}$ at 0° found by the first method in Section III. From the very close approximation to equality between $\frac{J}{\mu}$ and $\frac{1}{E}+t$, which our experiments have established, we may be sure that temperature from the freezing-point by the new system must agree to a very minute fraction of a degree with Centigrade temperature between the two prescribed points of agreement, 0° and 100°, and we may consider it as highly probable that there will also be a very close agreement through a wide range on each side of these limits. It becomes of course an object of the greatest importance, when the new system is adopted, to compare it with the old standard; and this is in fact what is substituted for the problem, the evaluation of Carnot's function, now that it is proposed to call the reciprocal of Carnot's function, temperature. In the next Section we shall see by what kind of examination of the physical properties of air this is to be done, and investigate an empirical formula expressing them consistently with all the experimental data as yet to be had, so far as we know. The following Table, showing the indications of the constant-volume and constant-pressure air-thermometer in comparison for every twenty degrees of the new scale, from the freezing-point to 300° above it, has been calculated from the formulæ (9), (10), and (39) of Section V. below.

Comparison of Air-thermometer with Absolute Scale.

Temperature by absolute scale in Cent. degrees from the freezing-point. $t-273{\cdot}7$.	Temperature Centigrade by constant-volume thermometer with air of specific gravity $\frac{\Phi}{v}$. $t=100\frac{p_t-p_{273{\cdot}7}}{p_{373{\cdot}7}-p_{273{\cdot}7}}$.	Temperature Centigrade by constant-pressure air-thermometer $\vartheta=100\frac{v_t-v_{273{\cdot}7}}{v_{373{\cdot}7}-v_{273{\cdot}7}}$.
° 0	° 0	° 0
20	$20+{\cdot}0298\times\frac{\Phi}{v}$ „	$20+{\cdot}0404\times\frac{p}{\Pi}$ „
40	40+·0403 „	40+·0477 „
60	60+·0366 „	60+·0467 „
80	80+·0223 „	80+·0277 „
100	100+·0000 „	100+·0000 „
120	120−·0284 „	120−·0339 „
140	140−·0615 „	140−·0721 „
160	160−·0983 „	160−·1134 „
180	180−·1382 „	180−·1571 „
200	200−·1796 „	200−·2018 „
220	220−·2232 „	220−·2478 „
240	240−·2663 „	240−·2932 „
260	260−·3141 „	260−·3420 „
280	280−·3610 „	280−·3897 „
300	300−·4085 „	300−·4377 „

The standard defined by REGNAULT is that of the constant-volume air-thermometer, with air at the density which it has when at the freezing-point under the pressure of 760 mm. or 22·9218 inches of mercury, and its indications are shown in comparison with the absolute scale by taking $\frac{\Phi}{v}=1$ in the second column of the preceding Table. The greatest discrepance between 0° and 100° Cent. amounts to less than $\frac{1}{30}$th of a degree, and the discrepance at 300° Cent. is only four-tenths. The discrepancies of the constant-pressure air-thermometer, when the pressure is equal to the standard atmospheric pressure, or $\frac{p}{\Pi}=1$, are somewhat greater, but still very small.

SECTION V. *Physical Properties of Air expressed according to the absolute Thermodynamic scale of Temperature.*

All the physical properties of a fluid of given constitution are completely fixed when its density and temperature are specified; and as it is these qualities which we can most conveniently regard as being immediately adjustable in any arbitrary manner, we shall generally consider them as the independent variables in formulæ expressing the pressure, the specific heats, and other properties of the particular fluid in any physical condition.

Let v be the volume (in cubic feet) of a unit mass (one pound) of the fluid, and t its absolute temperature; and let p be its pressure in the condition defined by these elements.

Let also e be the "mechanical energy*" of the fluid, reckoned from some assumed standard or zero state, that is, the sum of the mechanical value of the heat communicated to it, and of the work spent on it, to raise it from that zero state to the condition defined by (v, t); and let N and K be its specific heats with constant volume, and with constant pressure, respectively. Then denoting, as before, the mechanical equivalent of the thermal unit by J, and the value of CARNOT's function for the temperature t by μ, we have†

$$\frac{de}{dv}=\frac{J}{\mu}\frac{dp}{dt}-p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$N=\frac{1}{J}\frac{de}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$K=\frac{1}{J}\frac{de}{dt}+\frac{1}{J}\left(\frac{de}{dv}+p\right)\frac{\frac{dp}{dt}}{-\frac{dp}{dv}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From these we deduce, by eliminating e,

$$K-N=\frac{1}{\mu}\frac{\left(\frac{dp}{dt}\right)^2}{-\frac{dp}{dv}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\frac{dN}{dv}=\frac{d\left(\frac{1}{\mu}\frac{dp}{dt}\right)}{dt}-\frac{1}{J}\frac{dp}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

equations which express two general theorems regarding the specific heats of any fluid whatever, first published‡ in the Transactions of the Royal Society of Edinburgh, March 1851. The former (4) is the extension of a theorem on the specific heats of gases originally given by CARNOT§, while the latter (5) is inconsistent with one of his fundamental assumptions, and expresses in fact the opposed axiom of the Dynamical Theory. The use of the absolute thermo-dynamic system of thermometry proposed in Section IV., according to which the definition of temperature is

$$t=\frac{J}{\mu}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

simplifies these equations, and they become

$$JK-JN=t\frac{\left(\frac{dp}{dt}\right)^2}{-\frac{dp}{dv}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\frac{d(JN)}{dv}=t\frac{d^2p}{dt^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

* Dynamical Theory of Heat, Part V.—On the Quantities of Mechanical Energy contained in a Fluid in different States as to Temperature and Density, § 82. Trans. Roy. Soc. Edin., Dec. 15, 1851.

† Ibid. §§ 89, 91.

‡ Ibid. §§ 47, 48.

§ See "Account of CARNOT's Theory," Appendix III. Trans. Roy. Soc. Edin., April 30, 1849, p. 565.

To compare with the absolute scale the indications of a thermometer in which the particular fluid (which may be any gas, or even liquid) referred to in the notation p, v, t, is used as the thermometric substance, let p_0 and p_{100} denote the pressures which it has when at the freezing and boiling points respectively, and kept in constant volume, v; and let v_0 and v_{100} denote the volumes which it occupies under the same pressure, p, at those temperatures. Then if θ and ϑ denote its thermometric indications when used as a constant-volume and as a constant-pressure thermometer respectively, we have

$$\theta = 100\frac{p-p_0}{p_{100}-p_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\vartheta = 100\frac{v-v_0}{v_{100}-v_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Let also ϵ denote the "coefficient of increase of elasticity with temperature*," and $\mathfrak{s}$ the coefficient of expansion at constant pressure, when the gas is in the state defined by (v, t); and let E and $\mathcal{E}$ denote the mean values of the same coefficients between 0° and 100° Cent. Then we have

$$\epsilon = \frac{dp}{p_0\,dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\mathfrak{s} = \frac{\frac{dp}{dt}}{v_0 \times -\frac{dp}{dv}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\mathrm{E} = \frac{p_{100}-p_0}{100\,p_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\mathcal{E} = \frac{v_{100}-v_0}{100\,v_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Lastly, the general expression for $\frac{J}{\mu}$ quoted in Section II. from our paper of last year, leads to the following expression for the cooling effect on the fluid when forced through a porous plug as in our air experiments :—

$$\delta = \frac{1}{JK}\left\{\int_v^{v'}\left(t\frac{dp}{dt}-p\right)dv + (\mathrm{P'V'}-\mathrm{PV})\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

(p, v) $(\mathrm{P'}, \mathrm{V'})$ (P, V), as explained above, having reference to the fluid in different states of density, but always at the same temperature, t, as that with which it enters the plug.

From these equations, it appears that if p be fully given in terms of v and absolute values of t for any fluid, the various properties denoted by

$$\mathrm{JK}-\mathrm{JN}, \quad \frac{d(\mathrm{JN})}{dv}, \quad \theta, \quad \vartheta, \quad \epsilon, \quad \mathfrak{s}, \quad \mathrm{E}, \quad \mathcal{E}, \quad \text{and } \delta,$$

may all be determined for it in every condition. Conversely, experimental investiga-

* So called by Mr. Rankine. The same element is called by M. Regnault the coefficient of dilatation of a gas at constant volume.

tions of these properties may be made to contribute, along with direct measurements of the pressure for various particular conditions of the pressure, towards completing the determination of the function which expresses this element in terms of v and t. But it must be remarked, that even complete observations determining the pressure for every given state of the fluid, could give no information as to the values of t on the absolute scale, although they might afford data enough for fully expressing p in terms of the volume and the temperature with reference to some particular substance used thermometrically. On the other hand, observations on the specific heats of the fluid, or on the thermal effects it experiences in escaping through narrow passages, may lead to a knowledge of the absolute temperature, t, of the fluid when in some known condition, or to the expression of p in terms of v, and absolute values of t; and accordingly the formulæ (7), (8), and (15) contain t explicitly, each of them in fact essentially involving Carnot's function. As for actual observations on the specific heats of air, none which have yet been published appear to do more than illustrate the theory, by confirming (as Mr. Joule's, and the more precise results more recently published by M. Regnault, do), within the limits of their accuracy, the value for the specific heat of air under constant pressure which we calculated* from the *ratio of the specific heats*, determined according to Laplace's theory by observations on the velocity of sound, and the *difference of the specific heats* determined by Carnot's theorem with the value of Carnot's function estimated from Mr. Joule's original experiments on the changes of temperature produced by the rarefaction and condensation of air†, and established to a closer degree of accuracy by our preliminary experiments on expansion through a resisting solid‡. It ought also to be remarked, that the specific heats of air can only be applied to the evaluation of absolute temperature with a knowledge of the mechanical equivalent of the thermal unit; and therefore it is probable that, even when sufficiently accurate direct determinations of the specific heats are obtained, they may be useful rather for a correction or verification of the mechanical equivalent, than for the thermometric object. On the other hand, a comparatively very rough approximation to JK, the mechanical value of the specific heat of a pound of the fluid, will be quite sufficient to render our experiments on the cooling effects available for expressing with much accuracy, by means of the formula (15), a thermo-dynamic relation between absolute temperature and the mechanical properties of the fluid at two different temperatures.

Let us now assume

$$p=\frac{1}{v}\left\{At+\varphi_0(v)+\frac{\varphi_1(v)}{t}+\frac{\varphi_2(v)}{t^2}+\&c.\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

as an empirical formula, where A is a constant and $\varphi_0(v)$, $\varphi_1(v)$, &c. are functions of the volume to be determined by comparisons with experimental results. In doing so

* Philosophical Transactions, March 1852, p. 82.

† Royal Society Proceedings, June 20, 1844; or Phil. Mag., May 1845. ‡ Ibid. Dec. 1850.

we adopt the form to which Mr. RANKINE was led by his theory of molecular vortices, and which he has used with so much success for the expression of the pressure of saturated steam and the mechanical properties of gases; with this difference, that the series we assume proceeds in descending powers of the absolute thermo-dynamic temperature, while Mr. RANKINE's involves similarly the temperature according to what he calls "the scale of the perfect gas-thermometer."

Now any variable part of $\varphi_0(v)$, and the whole series of terms following it, must correspond to deviations from the gaseous laws, since the general expression of these laws would be simply $pv=At+B$, if A and B be constant. Hence for atmospheric air any variable part that $\varphi_0(v)$ can have, and all the terms following it in the series, must be very small fractions of pv. We shall see immediately that the various deviations from the gaseous laws which have been established by experiment, as well as the cooling effects which we have observed, are all such as to be represented by expressions derived from the preceding formula, if the variable part of $\varphi_0(v)$, and the whole functions $\varphi_1(v)$, $\varphi_2(v)$, &c. be taken each of them simply proportional to the density directly, or to the volume (v) of a pound inversely. We may then, to avoid unnecessary complications, at once assume

$$pv=At+B+\left(C+\frac{D}{t}+\frac{G}{t^3}\right)\frac{\Phi}{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where A, B, C, D and G are all constants to be determined by the comparison with experimental results, and Φ denotes a particular volume corresponding to a standard state of density, which it will be convenient to take as 12·387 cubic feet, the volume of a pound when under the atmospheric pressure Π (=2117 lbs. per square foot) of 29·9218 inches of mercury in latitude 45°. The series is stopped at the fifth term, because we have not at present experimental data for determining the coefficients for more. The experimental data which we have, and find available, are (1) the results of REGNAULT's observations on the coefficients of expansion at different constant densities, (2) the results of his observations on the compressibility, at a temperature of 4°·75 Cent., and (3) our own experimental results now communicated to the Royal Society. These are expressed within their limits of accuracy (at least for pressures of from one to five or six atmospheres, such as our experiments have as yet been confined to), by the following equations:—

$$E=\cdot003665+\frac{\cdot0000441}{3\cdot81}\left(\frac{\Phi}{v}-1\right),$$

or

$$E=\cdot00365343+\cdot000011575\,\frac{\Phi}{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$PV-P'V'=\cdot008163\,\frac{P-P'}{\Pi}\,PV, \text{ at temperature } 4°\cdot75 \text{ Cent.}, \quad . \quad . \quad . \quad (19)$$

and

$$\delta=\cdot26\,\frac{P-P'}{\Pi}, \text{ at temperature } 17° \text{ Cent.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Now, by the empirical formula (17), with equations (13) and (15), neglecting squares and products of the small quantities C, D, G, we find

$$\left.\begin{aligned} E&=\frac{100\,A-\left\{D\left(\frac{1}{t_0}-\frac{1}{t_0+100}\right)+G\left[\frac{1}{t_0^2}-\frac{1}{(t_0+100)^2}\right]\right\}\frac{\Phi}{v}}{100\left\{At_0+B+\left(C+\frac{D}{t_0}+\frac{G}{t_0^2}\right)\frac{\Phi}{v}\right\}}\\ &=\frac{A}{At_0+B}-\frac{1}{100(At_0+B)}\left\{\frac{100A}{At_0+B}\left(C+\frac{D}{t_0}+\frac{G}{t_0^2}\right)+D\left(\frac{1}{t_0}-\frac{1}{t_0+100}\right)+G\left(\frac{1}{t_0^2}-\frac{1}{(t_0+100)^2}\right)\right\}\frac{\Phi}{v}\end{aligned}\right\}\quad(21)$$

$$\left(\frac{P'V'-PV}{PV}\right)_{4\cdot75}=\frac{-\left(C+\frac{D}{t_{4\cdot75}}+\frac{G}{t^2_{4\cdot75}}\right)\left(\frac{\Phi}{V}-\frac{\Phi}{V'}\right)}{At_{4\cdot75}+B+\left(C+\frac{D}{t_{4\cdot75}}+\frac{G}{t^2_{4\cdot75}}\right)\frac{\Phi}{V}}=\frac{-\left(C+\frac{D}{t_{4\cdot75}}+\frac{G}{t^2_{4\cdot75}}\right)\left(\frac{\Phi}{V}-\frac{\Phi}{V'}\right)}{At_{4\cdot75}+B}\quad(22)$$

$$=-\frac{At_0+B}{(At_{4\cdot75}+B)^2}\left(C+\frac{D}{t_{4\cdot75}}+\frac{G}{t^2_{4\cdot75}}\right)\left(\frac{P}{\Pi}-\frac{P'}{\Pi}\right)\quad(23)$$

and

$$\delta=\frac{1}{JK}\left\{-B\log\frac{V'}{V}-\left(2C+\frac{3D}{t}+\frac{4G}{t^2}\right)\left(\frac{\Phi}{V}-\frac{\Phi}{V'}\right)\right\}\quad(24)$$

$$=\frac{1}{JK}\left\{-B\log\frac{P}{P'}-\frac{At_0+B}{At+B}\left(2C+\frac{3D}{t}+\frac{4G}{t^2}\right)\left(\frac{P}{\Pi}-\frac{P'}{\Pi}\right)\right\}.\quad(25)$$

From the last, and the equation of condition (20), we find

$$B=0\quad(26)$$

and

$$-\frac{1}{JK}\,\frac{t_0}{t_0+17}\left(2C+\frac{3D}{t_0+17}+\frac{4G}{t_0+17}\right)=\cdot26.\quad(27)$$

Again, by equations (21) and (18) similarly used, we have

$$\frac{A}{At_0+B}=\cdot00365343\quad(28)$$

and

$$\frac{-1}{100(At_0+B)}\left\{\frac{100A}{At_0+B}\left(C+\frac{D}{t_0}+\frac{G}{t_0^2}\right)+D\left(\frac{1}{t_0}-\frac{1}{t_0+100}\right)+G\left(\frac{1}{t_0^2}-\frac{1}{(t_0+100)^2}\right)\right\}=\cdot000011575.\quad(29)$$

From (26) and (28), we have

$$\left.\begin{aligned}\frac{1}{t_0}&=\cdot00365343\\ \text{and}\quad t_0&=273^\circ\cdot72\end{aligned}\right\}\quad(30)$$

That is, from the thermo-dynamic experimental result (20), and the experimental result (18) characteristic of the difference of temperature which we choose to call 100 from the freezing-point upwards, showing the effect on the pressure of air, we have determined the absolute thermo-dynamic temperature of the freezing-point. The result agrees within one-twentieth of a degree with that which we obtained in Section II. by the first plan, in which the same data as regards the increase of pressure of air from t_0 to t_0+100° were used, but taken into account on different and apparently less satisfac-

tory principles. From (22) and its equation of condition (19) we derive only a single equation among the constants, which is as follows:—

$$-\frac{At_0+B}{(At_{4\cdot75}+B)^2}\left(C+\frac{D}{t_{4\cdot75}}+\frac{G}{t^2_{4\cdot75}}\right)=\cdot008163. \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Another equation besides the three, (27), (29), and (31), is required to determine the four remaining unknown constants, A, C, D, G; and is afforded by a determination of the density of air, which has been most accurately given by REGNAULT, who finds that the weight of 26224 cubic feet of air at constant temperature 0° Cent. and constant atmospheric pressure, in lat. 45°, amounts to the same as the pressure per square foot, a result which is expressed by the equation

$$\Pi\Phi=26224.$$

Here Π denotes the value of p in the empirical formula (17), which corresponds to $t=t_0$, (the absolute temperature of the freezing-point,) and $v=\Phi$. Hence we have the equation

$$At_0+B+C+\frac{D}{t_0}+\frac{G}{t^2_0}=26224. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

Calling 26224, H, (the "height of the homogeneous atmosphere") for brevity, and denoting the true value of At_0 by $\mathfrak{H}$, which must be very nearly equal to H, we may simplify the treatment of the four equations by taking the approximate value H for At_0, in three of them, (27), (29), (31), without losing accuracy, and we may afterwards use (32) to determine the exact value of $\mathfrak{H}$. Accordingly (and to avoid subsequent confusion of algebraic signs in the numerical results) it is convenient to assume

$$C=-\mathfrak{H}\alpha, \quad D=\mathfrak{H}\beta, \quad G=-\mathfrak{H}\gamma. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Then, taking everywhere B=0 as we have found it, we have, instead of (32), (27), (29), (31) respectively,

$$\mathfrak{H}\left(1-\alpha+\frac{\beta}{t_0}-\frac{\gamma}{t^2_0}\right)=H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

$$2\alpha-\frac{3\beta}{t_0+17}+\frac{4\gamma}{(t_0+17)^2}=\frac{JK}{H}\cdot\frac{t_0+17}{t_0}\times\cdot26 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

$$100\,\alpha-\left(\frac{100}{t_0}+1-\frac{t_0}{t_0+100}\right)\beta+\left(\frac{100}{t^2_0}+\frac{1}{t_0}-\frac{t_0}{(t_0+100)^2}\right)\gamma=100t_0\times\cdot000011575 \quad . \quad (36)$$

and

$$\alpha-\frac{\beta}{t_0+4\cdot75}+\frac{\gamma}{(t+4\cdot75)^2}=\left(\frac{t_0+4\cdot75}{t_0}\right)^2\times\cdot008163. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Reducing to numbers the coefficients of α, β, γ, and the other terms, by using the value 273·72 found above (30) for t_0; 1390 for J; and ·238 for K according to the observations and theoretical conclusion regarding the absolute value of the specific heat of air under constant pressure, published in Notes to Mr. JOULE's paper on the

Air-Engine, since confirmed by REGNAULT's observations; we have three simple equations for determining the three unknown quantities, α, β, γ; and then a single simple equation (34) for determining $\mathfrak{H}$. By solving these, we find

$$\left.\begin{aligned}\alpha &= \cdot 0012811\\ \beta &= 1\cdot 3918\\ \gamma &= 353\cdot 20\\ \mathfrak{H} &= 26247\cdot 9\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (38)$$

Using these and (33) in (17), we have

$$pv = \mathrm{H}\left\{t - \left(\cdot 0012811 - \frac{1\cdot 3918}{t} + \frac{353\cdot 2}{t^2}\right)\frac{\Phi}{v}\right\}, \quad \ldots\ldots\ldots \quad (39)$$

an empirical formula which represents the pressure of air, in terms of its temperature on the absolute thermo-dynamic scale and its density, consistently with REGNAULT's observations on the increase of pressure from 0° to 100° Cent. and on the compressibility at 4°·75 Cent., and consistently with our own on the thermal effects of air at the temperature 17° Cent., forced with various pressures through a porous body.

It also agrees perfectly with REGNAULT's observations on the expansion of air under constant pressure.

The only other observations on the variations of pressure and density available for testing the formula, are REGNAULT's comparisons of different air-thermometers. The Table at the end of Section IV., which has been calculated from our empirical formula (39), shows, in its second and third columns, the indications to be expected of constant-volume and of constant-pressure air-thermometers in terms of temperature on the absolute thermo-dynamic scale; and the differences between the numbers show the discrepancies to be expected between different air-thermometers themselves. These discrepancies, although considerably greater than have been observed by REGNAULT on thermometers with air at different densities or pressures of from half to double those of the standard, appear to be within, or scarcely to exceed, the limits of errors of observation. If further examination of this subject proves that there is in reality a closer agreement between air-thermometers than shown in the Table, it will be necessary to introduce another equation of condition to reconcile them, and to determine another constant in the general empirical formula for p. At present however we do not think it necessary to take up this question, as we hope soon to have much more extensive experimental data on the cooling effects, with more varied pressures and at different temperatures; which should both show whether any other functions of the density than that of simple proportionality will be required, and enable us to determine other terms of the series in descending powers of t, and will so give us probably a much more exact empirical formula for air than all the data at present available enable us to obtain.

We have also calculated formulæ for the specific heats of air under constant pressure and constant volume, by which the variations of these elements with the tempe-

rature and density are determined. Should they turn out to be inconsistent with facts, other equations of condition will have to be introduced and other constants of the empirical formula determined, to do away with the discrepancies; but probably no experiments have yet been made of sufficient accuracy to test them.

The following expressions are derived from the general equations (7) and (8) for the mechanical values of the specific heats of a fluid, by substituting for p the particular expressions for the case of air afforded by the empirical formula (39), and integrating the second of the two results with reference to v:—

$$J(K-N)=\frac{\mathfrak{H}}{t_0}+\frac{2H}{t}\left(\alpha-\frac{2\beta}{t}+\frac{3\gamma}{t^2}\right)\frac{\Phi}{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$$JN=J\mathfrak{N}+\frac{2H}{t}\left(\frac{-\beta}{t}+\frac{3\gamma}{t^2}\right)\frac{\Phi}{v}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

in the second of which, $J\mathfrak{N}$ denotes the value of JN when $v=\infty$. Using a similar notation $J\mathfrak{K}$ with reference to the specific heat of air at constant pressure, we have from these two equations,

$$J\mathfrak{K}=J\mathfrak{N}+\frac{\mathfrak{H}}{t_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

$$JK=J\mathfrak{K}+\frac{2H}{t}\left(\alpha-\frac{3\beta}{t}+\frac{6\gamma}{t^2}\right)\frac{\Phi}{v}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

or with $\frac{p}{\Pi}\frac{t_0}{t}$ instead of $\frac{\Phi}{v}$,

$$JK=J\mathfrak{K}+\frac{2Ht_0}{t^2}\left(\alpha-\frac{3\beta}{t}+\frac{6\gamma}{t^2}\right)\frac{p}{\Pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

Lastly, denoting the ratio of the specific heats, $\frac{K}{N}$, by k, and the particular value, $\frac{\mathfrak{K}}{\mathfrak{N}}$, corresponding to the case of extreme dilatation, by $\mathfrak{k}$, we have, to the same degree of approximation as the other expressions,

$$k=\mathfrak{k}+\frac{2H}{JNt}\left\{\alpha-\frac{(3-k)\beta}{t}+\frac{(6-3k)\gamma}{t^2}\right\}\frac{\Phi}{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

In the Notes to Mr. Joule's paper on the Air-Engine*, it was shown that if Mayer's hypothesis be true we must have approximately,

$$K=\cdot2374 \text{ and } N=\cdot1684,$$

because observations on the velocity of sound, with Laplace's theory, demonstrate that

$$k=1\cdot410$$

within $\frac{1}{700}$ of its own value. Now the experiments at present communicated to the Royal Society prove a very remarkable approximation to the truth in that hypothesis (see above, Section I.), and we may therefore use these values as very close approximations to the specific heats of air. The experiments on the friction of fluids and solids

* Philosophical Transactions, March 1852, p. 82.

made for the purpose of determining the mechanical value of heat*, give for J the value 1390; and we therefore have JN=234·1 with sufficient accuracy for use in calculating small terms. Calculating accordingly, with this for JN, and with the value 1·41 for k, the coefficient of $\frac{\Phi}{v}$ in (45), we find,

$$\left.\begin{array}{ll} \text{for} & t=273\cdot7 \text{ (temperature 0° Cent.)}, \quad k=\mathfrak{k}+\cdot00126\times\frac{\Phi}{v} \\ \text{and for} & t=293\cdot7 \text{ (temperature 20° Cent.)}, \quad k=\mathfrak{k}+\cdot00076\times\frac{\Phi}{v} \end{array}\right\} \quad . \quad . \quad . \quad . \quad (46)$$

Now according to Regnault we have, for dry air at the freezing-point, in the latitude of Paris,

$$H=26215;$$

and since the force of gravity at Paris, with reference to a foot as the unit of space and a second as the unit of time, is 32·1813, it follows that the velocity of sound in dry air at 0° Cent. would be, according to Newton's unmodified theory,

$$\sqrt{26215\times32\cdot1813}=918\cdot49,$$

or in reality, according to Laplace's theory,

$$\sqrt{k}.\sqrt{26215\times32\cdot1813}.$$

But according to Bravais and Martins it is in reality

1090·5, which requires that $k=1\cdot4096$,

or according to Moll and Van Beck

1090·1, which requires that $k=1\cdot4086$.

The mean of these values of k is 1·4091. If this be the true value of k for 0° Cent. and the standard density $\left(\frac{\Phi}{v}=1\right)$, the correction shown in (46) above would give

$$\mathfrak{k}=1\cdot40784;$$

or if it be the true value of k for air of the standard density, and the temperature 20° Cent., the correction will give

$$\mathfrak{k}=1\cdot40834.$$

Which of these hypotheses is most near the truth, might possibly be ascertained by reference to the original observations on the velocity of sound from which the preceding results reduced to the temperature 0° were obtained, but as the actual temperatures of the air must in all probability have been between 0° and 20° Cent., without going into the details of the calculations by which the reductions to 0° have been made, we may feel confident that $\mathfrak{k}$ cannot differ much from either of the two preceding estimates, and we may take their mean,

$$\mathfrak{k}=1\cdot4081, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

as probably a very close approximation to the truth. Now we have seen above that

* Philosophical Transactions, 1849.

$\mathfrak{k}=26247{\cdot}9$, and since $t_0=273{\cdot}7$, we have, by (42),

$$\mathrm{J}\mathfrak{k}-\mathrm{J}\mathfrak{B}=95{\cdot}9003. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

From this, and the preceding value of $\mathfrak{k}$ $\left(\text{or } \frac{\mathfrak{K}}{\mathfrak{B}}\right)$, we have

$$\left.\begin{aligned}\mathrm{J}\mathfrak{B}&=134{\cdot}9921\\ \mathrm{J}\mathfrak{k}&=330{\cdot}8924\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

Using these, and the values of α, β, and γ obtained above, in the preceding expressions (40), (41), (45) and (44), and calculating for every 20° of temperature from 0° Cent. to 300°, we obtain the results shown in the following Table; the assumptions

$$\left.\begin{aligned}f&=\frac{2\mathrm{H}}{t}\left(\alpha-\frac{2\beta}{t}+\frac{3\gamma}{t^2}\right)\\ g&=\frac{2\mathrm{H}}{t}\left(\frac{-\beta}{t}+\frac{3\gamma}{t^2}\right)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

being made merely for convenience in exhibiting the formulæ and mode of calculation along with the results.

Table of the Specific Heats of Air.

Temperature from freezing-point, $t-t_0$.	I. Difference of mechanical values of specific heats, $\mathrm{JK}-\mathrm{JN}=\frac{\mathfrak{W}}{t_0}+f\frac{\Phi}{v}$.	II. Mechanical value of specific heat at constant volume, $\mathrm{JN}=\mathrm{J}\mathfrak{B}+g\frac{\Phi}{v}$.	III. Ratio of specific heats, $k=\mathfrak{k}+\frac{1}{\mathrm{J}\mathfrak{B}}(f+g-kg)\frac{\Phi}{v}$.	IV. Mechanical value of specific heat at constant pressure, $\mathrm{JK}=\mathrm{J}\mathfrak{K}+\frac{t_0}{t}(f+g)\frac{p}{\Pi}$
°				
0	$95{\cdot}9003+1{\cdot}0080\times\frac{\Phi}{v}$	$234{\cdot}9921+1{\cdot}7376\times\frac{\Phi}{v}$	$1{\cdot}4081+{\cdot}001262\times\frac{\Phi}{v}$	$330{\cdot}8924+2{\cdot}7457\times\frac{p}{\Pi}$
20	$95{\cdot}9003+{\cdot}7306$ „	$234{\cdot}9921+1{\cdot}3486$ „	$1{\cdot}4081+{\cdot}000759$ „	$330{\cdot}8924+1{\cdot}9376$ „
40	$95{\cdot}9003+{\cdot}5314$ „	$234{\cdot}9921+1{\cdot}0594$ „	$1{\cdot}4081+{\cdot}000404$ „	$330{\cdot}8924+1{\cdot}3880$ „
60	$95{\cdot}9003+{\cdot}3862$ „	$234{\cdot}9921+{\cdot}8408$ „	$1{\cdot}4081+{\cdot}000177$ „	$330{\cdot}8924+1{\cdot}0064$ „
80	$95{\cdot}9003+{\cdot}2792$ „	$234{\cdot}9921+{\cdot}6731$ „	$1{\cdot}4081+{\cdot}000014$ „	$330{\cdot}8924+{\cdot}7369$ „
100	$95{\cdot}9003+{\cdot}1994$ „	$234{\cdot}9921+{\cdot}5426$ „	$1{\cdot}4081-{\cdot}000098$ „	$330{\cdot}8924+{\cdot}5435$ „
120	$95{\cdot}9003+{\cdot}1396$ „	$234{\cdot}9921+{\cdot}4401$ „	$1{\cdot}4081-{\cdot}000175$ „	$330{\cdot}8924+{\cdot}4030$ „
140	$95{\cdot}9003+{\cdot}0944$ „	$234{\cdot}9921+{\cdot}3587$ „	$1{\cdot}4081-{\cdot}000225$ „	$330{\cdot}8924+{\cdot}2997$ „
160	$95{\cdot}9003+{\cdot}0601$ „	$234{\cdot}9921+{\cdot}2934$ „	$1{\cdot}4081-{\cdot}000256$ „	$330{\cdot}8924+{\cdot}2331$ „
180	$95{\cdot}9003+{\cdot}0345$ „	$234{\cdot}9921+{\cdot}2412$ „	$1{\cdot}4081-{\cdot}000275$ „	$330{\cdot}8924+{\cdot}1663$ „
200	$95{\cdot}9003+{\cdot}0141$ „	$234{\cdot}9921+{\cdot}1977$ „	$1{\cdot}4081-{\cdot}000285$ „	$330{\cdot}8924+{\cdot}1223$ „
220	$95{\cdot}9003-{\cdot}0010$ „	$234{\cdot}9921+{\cdot}1625$ „	$1{\cdot}4081-{\cdot}000288$ „	$330{\cdot}8924+{\cdot}0895$ „
240	$95{\cdot}9003-{\cdot}0125$ „	$234{\cdot}9921+{\cdot}1334$ „	$1{\cdot}4081-{\cdot}000286$ „	$330{\cdot}8924+{\cdot}0644$ „
260	$95{\cdot}9003-{\cdot}0211$ „	$234{\cdot}9921+{\cdot}1094$ „	$1{\cdot}4081-{\cdot}000282$ „	$330{\cdot}8924+{\cdot}0453$ „
280	$95{\cdot}9003-{\cdot}0275$ „	$234{\cdot}9921+{\cdot}0893$ „	$1{\cdot}4081-{\cdot}000274$ „	$330{\cdot}8924+{\cdot}0306$ „
300	$95{\cdot}9003-{\cdot}0322$ „	$234{\cdot}9921+{\cdot}0726$ „	$1{\cdot}4081-{\cdot}000263$ „	$330{\cdot}8924+{\cdot}0193$ „

The mean value of JK for air at constant pressure p, and for the range of temperature from t' to t obtained by integrating equation (44) with reference to t between those limits, and dividing by $t-t'$, is

$$\mathrm{JK}+\frac{\mathrm{HC}}{t-t'}\left\{2\alpha\left(\frac{1}{t'}-\frac{1}{t}\right)-3\beta\left(\frac{1}{t'^2}-\frac{1}{t^2}\right)+2\gamma\left(\frac{1}{t'^3}-\frac{1}{t^3}\right)\right\}\frac{p}{\Pi};$$

and this divided by J expresses the element actually observed in experiments such as

have hitherto been made on the specific heat of air at constant pressure. The theoretical results, according to this expression and to the determination 1390 for J, are as follow for several particular cases :—

Range of temperature.	Mean specific heat of air at atmospheric pressure.	Mean specific heat of air at five times the atmospheric pressure.
Cent. degrees.		
0 to 100	·2390	·2428
0 to 300	·2384	·2396

The comparison of these results with sufficiently accurate direct experiments on the specific heat of air at the atmospheric pressure, might lead to a correction on the value 1390 found for J by direct experiments on the generation of heat by friction; but it must depend on the evidence afforded by accounts of the experimental details, whether the value of the mechanical equivalent of the thermal unit is to be corrected from them, or whether we may assume the preceding results as nearer the truth than the results which they indicate. No such evidence, nor any demonstrating whether or not the influence of change of pressure is such as shown in the preceding Tables, has as yet been published.

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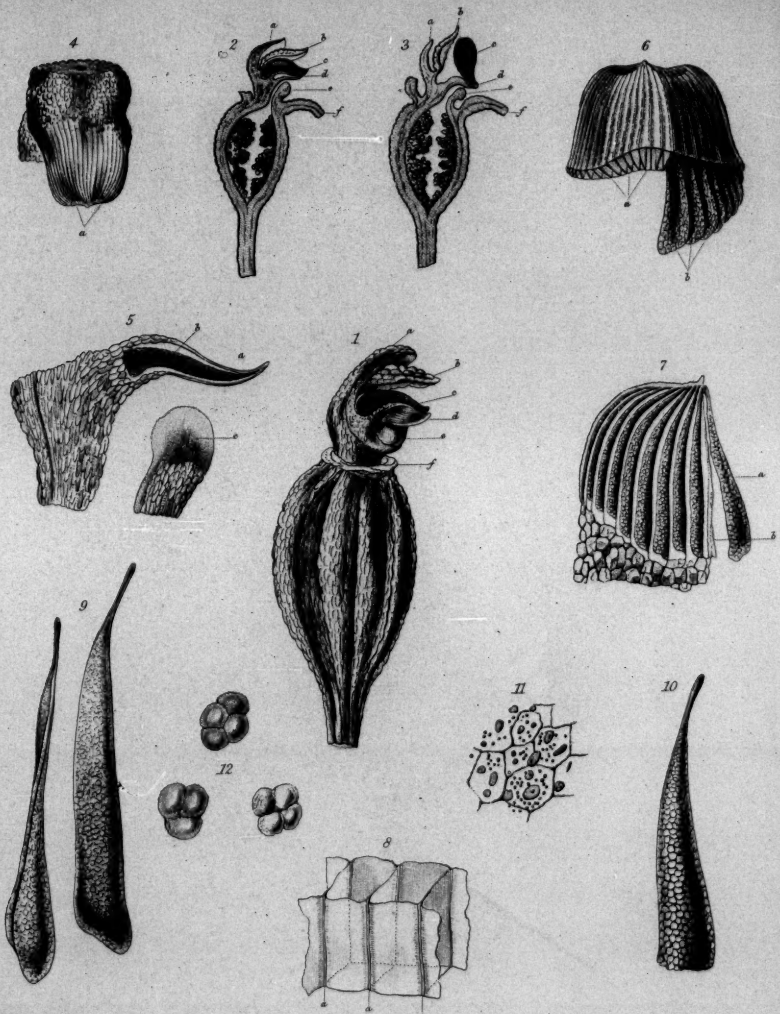

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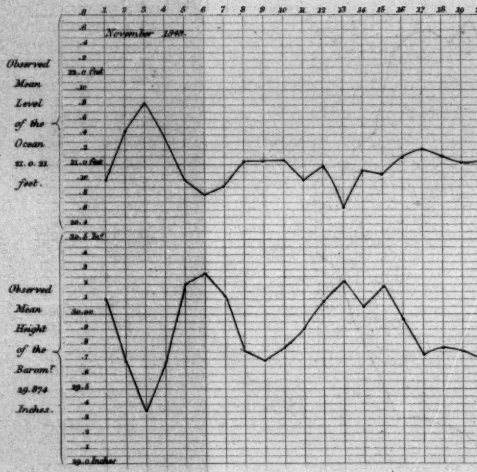
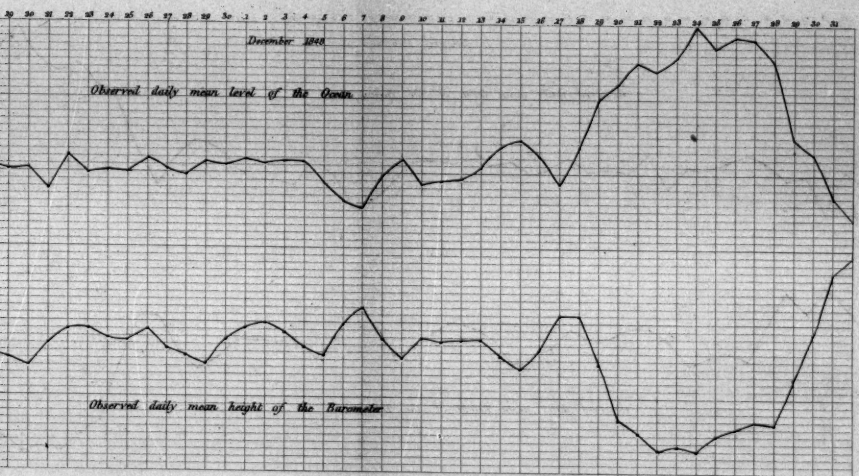

November 1849.
Observed Mean Level of the Ocean. 21. 0. 22. feet.
29.0 feet
Observed Mean Height of the Barom.r 29.874 Inches.
29.0 Inches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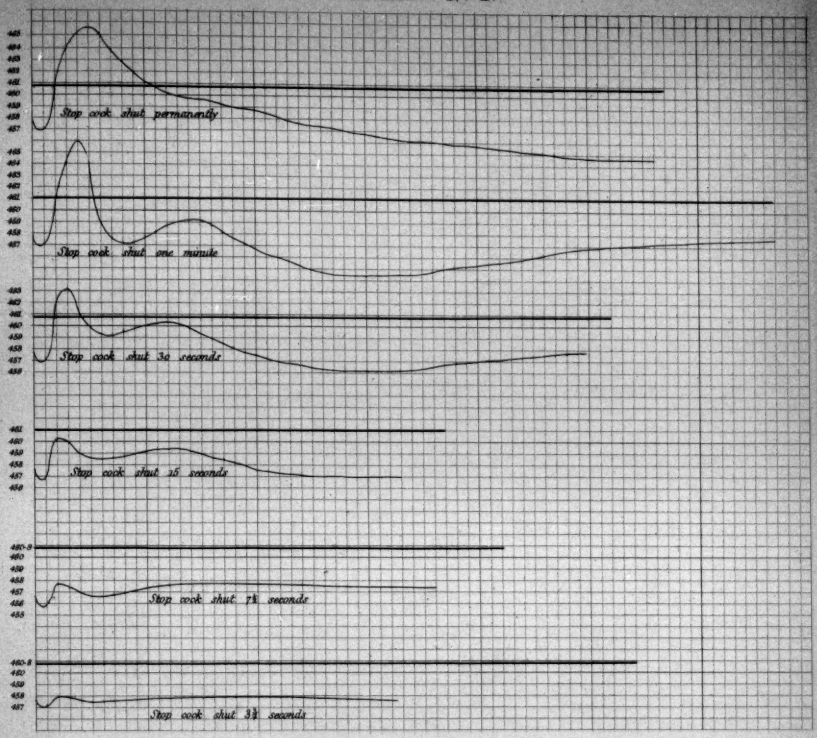
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Stop cock shut 30 seconds
Stop cock shut 15 seconds
Stop cock shut 7½ seconds
Stop cock shut 3¾ seconds

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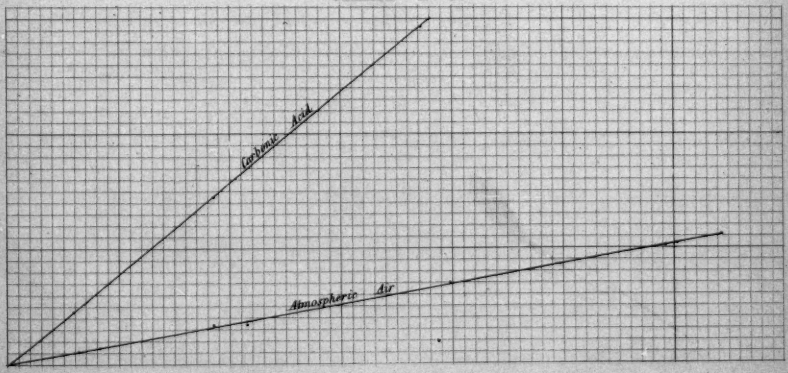

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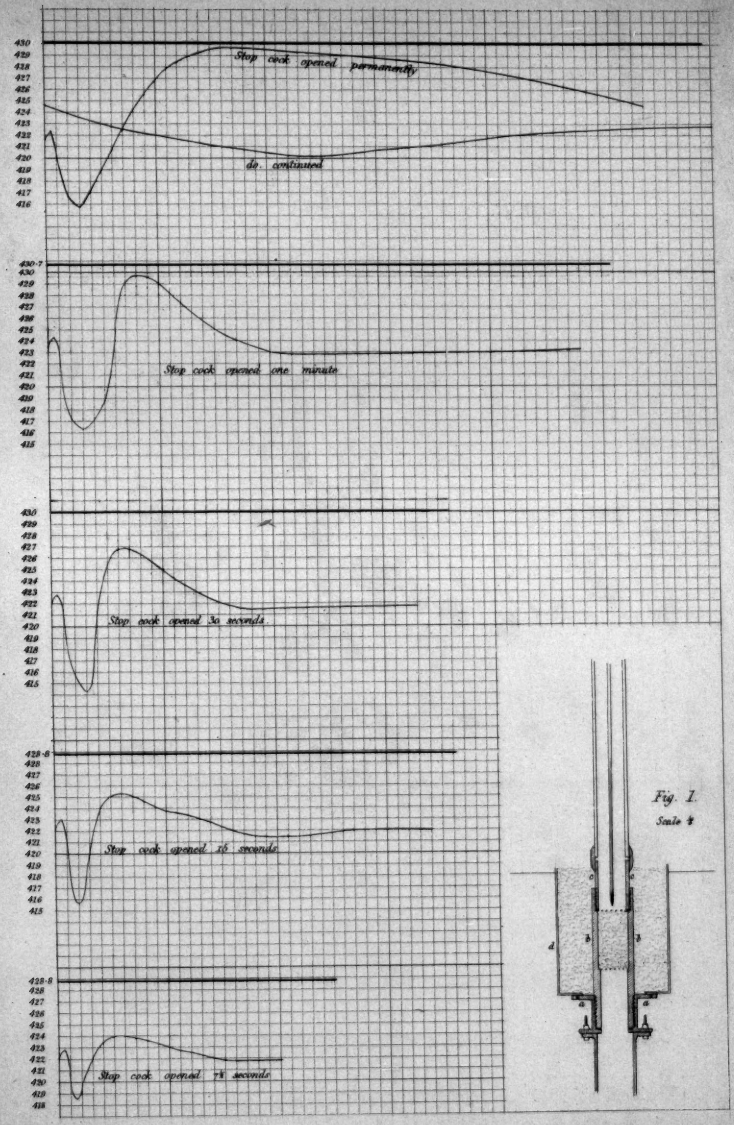
Stop cock opened permanently
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Stop cock opened 7½ seconds

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